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Papers

Artykuły

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Roman BABKO[1], Tatiana KUZMINA[2], Grzegorz ŁAGÓD[3]
and Katarzyna M. JAROMIN-GLEŃ[4]

THE PERIPHYTON COMMUNITIES OF A MUNICIPAL WASTEWATER TREATMENT PLANT

ZBIOROWISKA PERYFITONU MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW

Abstract: The study was undertaken to determine the composition of periphyton and its quantitative development during consecutive stages of wastewater treatment in a flow-type purification plant with the biological part serving as a modified Bardenpho system (Hajdow, Lublin, south-eastern Poland).The periphyton was sampled from the wastewater plant walls at all main stages of water purification. The following groups of organisms: algae, fungi, flagellates, testate amoeba, ciliates, rotifers, and nematodes were identified in the composition of periphyton. At the end of the purification process, the proportion of metazoa and protozoa in the periphyton of the successive chambers increased, while the abundance of flagellates declined. In all the sampling points studied, protozoa and metazoa formed the basis of the periphyton community and their proportion ranged from 75 to 95%.

Keywords: periphyton, communities, municipal wastewater treatment plant (WWTP), protozoa, metazoa

Introduction

The periphyton is observed on all surfaces submerged in water. The biofilm was studied mostly in purification systems, where it was the main instrument and process factor of sewage treatment. Many publications are devoted to studies of physical characteristics and physiological activity of biofilms and their bacterial component [1-4]. At the same time, a relatively small number of studies provide information concerning other organisms that together with bacteria are regular components of biofilm and have a certain influence on bacterial life activity and on the purification process performed by the biofilm community. For example, the paper by Madoni [5] contains data about biofilm protozoa from rotating biological contactors (RBC) and percolating filters. Results of studies of protozoa in percolating filters have been presented by some authors [6, 7]. Results of research of ciliate populations and their distribution in RBC systems can be found in papers [8-12]. There is also evidence that, besides bacteria, ciliates are the most numerous and important organisms in the biofilm of RBC [10, 11]. Metazoa are also an important part of biofilm community, since they often reach big quantities and are influential links of trophic chains [13, 14].

Today, there is not enough information to specify the role that periphyton plays in such treatment facilities as bioreactors with activated sludge working in the flow-mode or in SBRs. Much less is known about periphyton, *ie* a biofilm growing on the walls of

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[*] Contribution was presented during ECOpole'14 Conference, Jarnoltowek, 15-17.10.2014

purification facilities submerged in wastewater, than about activated sludge that is functioning in bioreactors. This paper presents the study of the structure of the main periphyton groups and their quantitative development at different stages of wastewater purification. The analysis of the structure dynamics and diversity of the main periphyton groups in each purification stage can provide additional information concerning stability of the aforementioned processes and probable destabilization of the activated sludge structure and properties.

Materials and methods

The research material comprised periphyton sampled from the main line of the technological system of the "Hajdow" mechanical-biological wastewater treatment plant in Lublin (south-eastern Poland). The analyses of the periphyton during the main stages of sewage purification were carried out in spring when activated sludge was not in optimal conditions. In the aeration chamber, the initial stages of activated sludge bulking and foaming were observed. The samples of the periphyton from the walls of the main chambers were analyzed to calculate the quantities of the major hydrobiont groups, such as flagellates, testate amoebae, rotifers, nematodes, ciliates, algae, and fungi. Ciliates were analyzed according to their ecological groups - attached ciliates, crawling ciliates, and swimming ciliates.

The samples were taken with a scraper ca. 15 cm below the sewage surface in each device. The periphyton was sampled from an area of approximately 100 cm^2. The sampling points included: 1 - screen chamber, 2 - grit chamber, 3 - primary clarifier, 4 - anaerobic chamber, 5 - anoxic chamber, 6 - aeration chamber, 7 - secondary clarifier, and 8 - recirculation channel. The data presented in the article are averaged from two months of the experiment with a one-week sampling period.

Results and discussion

During the study period, there was a tendency that the proportion of metazoa and protozoa in the periphyton of the successive chambers was increasing towards the end of the purification process (Fig. 1). Their percentage at the various purification stages ranged from 75 to 95%. Together with fungi, the proportion of heterotrophic organisms in the periphyton can reach 99%. The proportion of fungi in the various stages of purification was not higher than 8%, while autotrophic organisms formed from 1 to 25% of all organism abundance. Similar results were obtained in an RBC-type water treatment plant [11]. In such periphyton (RBC), ciliates constituted the most numerous group of organisms (55-95% of the total quantity). In the periphyton conditions of the Hajdow flow-type purification plant, ciliated protozoa make up from 14 to 69%.

In treatment facilities such as aeration chambers, activated sludge usually operates on the basis of heterotrophic communities, and their autotrophic component is minimized. Therefore, the question of determination of the potential involvement of autotrophs in the periphyton of treatment plants is of great interest. The role of heterotrophic and autotrophic organisms in the periphyton structure in the conditions of the treatment plant is shown in Figure 2. There is a direct relation between the dynamics of algae, fluctuations in illumination intensity, and efficiency of the water clarification process. The quantitative representation of algae and fungi recorded at various points during this study is presented in Figure 3.

Quite an independent tendency was shown by testate amoebae and flagellates. The average values of testate amoebae abundance were decreasing insignificantly from the beginning until the end of the purification process. Simultaneously, this tendency in flagellates was quite explicit (Fig. 4). Since the beginning of the process, their abundance decreased by 30 times. It is obvious that small flagellates propagate fast in the water rich in organic matter and with minimum oxygen saturation. Thus, the flagellate dynamics will be rather determined by disturbances in the purification process or excessive inflow of wastewater. According to Curds [15], flagellates predominate in the system in the early stages because of their lower energy requirements. Heterotrophic flagellates are therefore recognized as indicators of malfunction of treatment facilities or their overload [5].

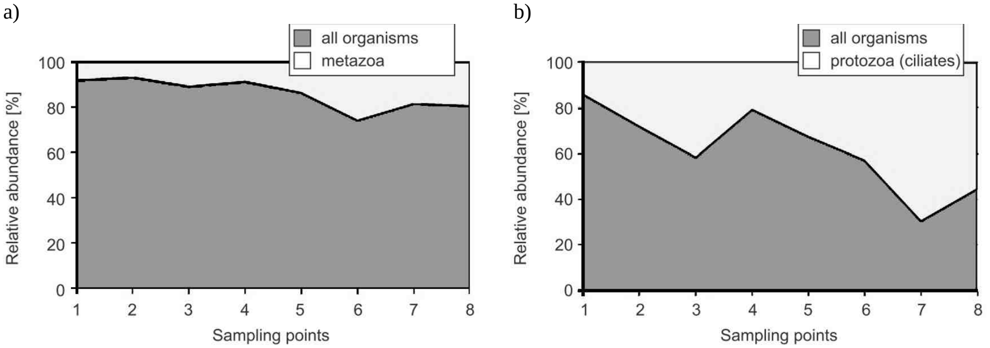

Fig. 1. Proportion of metazoa (a) and ciliates (b) in the total abundance of organisms in the periphyton along the treatment plant. Sampling points: 1 - screen chamber, 2 - grit chamber, 3 - primary clarifier, 4 - anaerobic chamber, 5 - anoxic chamber, 6 - aeration chamber, 7 - secondary clarifier, 8 - recirculation channel

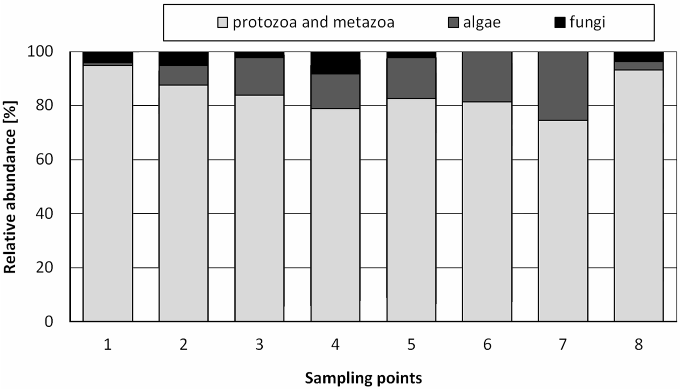

Fig. 2. The ratio of the quantitative representation of different groups of organisms in the structure of the periphyton community along the treatment plant. Sampling points: 1 - screen chamber, 2 - grit chamber, 3 - primary clarifier, 4 - anaerobic chamber, 5 - anoxic chamber, 6 - aeration chamber, 7 - secondary clarifier, 8 - recirculation channel

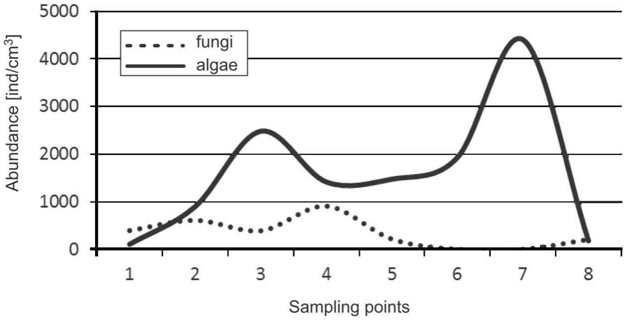

Fig. 3. Abundance of algae and fungi in the periphyton along the treatment plant. Sampling points: 1 - screen chamber, 2 - grit chamber, 3 - primary clarifier, 4 - anaerobic chamber, 5 - anoxic chamber, 6 - aeration chamber, 7 - secondary clarifier, 8 - recirculation channel

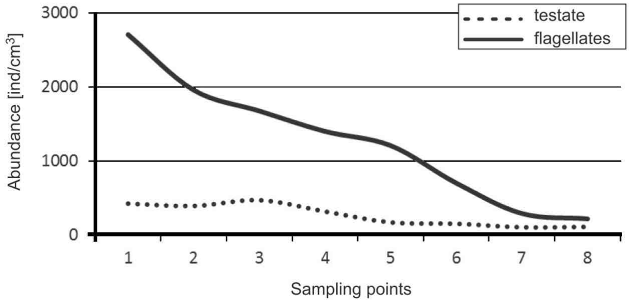

Fig. 4. Abundance of testate amoeba and flagellates in the periphyton along the treatment plant. Sampling points: 1 - screen chamber, 2 - grit chamber, 3 - primary clarifier, 4 - anaerobic chamber, 5 - anoxic chamber, 6 - aeration chamber, 7 - secondary clarifier, 8 - recirculation channel

Summary and conclusions

The periphyton community in the successive chambers of the flow-type treatment plant with the biological part functioning in the modified system Bardenpho reached maximum abundance in the primary and secondary clarifiers. Towards the end of the purification process of the periphyton in the successive chambers, the amount of protozoa and metazoa increased. In all the sampling points studied, the basis of the periphyton community was formed by protozoa and metazoa, which accounted for 75-95%. The proportion of heterotrophs reached 99% and that of autotrophs varied from 1 to 25%.

Acknowledgments

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ZBIOROWISKA PERYFITONU MIEJSKIEJ OCZYSZCZALNI ŚCIEKÓW

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Abstrakt: W pracy zaprezentowano badania składu peryfitonu i jego rozwój ilościowy podczas kolejnych etapów oczyszczania ścieków w miejskiej oczyszczalni ścieków Hajdów w Lublinie, której część biologiczna pracuje w technologii zmodyfikowanego systemu Bardenpho. Próbki peryfitonu pobierano z powierzchni ścian obiektów na wszystkich głównych etapach oczyszczania ścieków. W składzie peryfitonu zostały zidentyfikowane następujące grupy organizmów: glony, grzyby, wiciowce, ameby skorupkowe, orzęski, wrotki i nicienie. W kolejnych analizowanych urządzeniach zlokalizowanych w ciągu technologicznym oczyszczalni peryfiton wykazywał wzrost ilości organizmów w obrębie grup metazoa i pierwotniaków, podczas gdy liczebność wiciowców uległa zmniejszeniu. We wszystkich badanych punktach pomiarowych podstawa zbiorowisk peryfitonu utworzona była przez pierwotniaki i metazoa, ich udział wahał się od 75 do 95%.

Słowa kluczowe: peryfiton, zbiorowiska, komunalna oczyszczalnia ścieków, pierwotniaki, metazoa

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Krystyna CYBULSKA[1], Natalia SUCHECKA[1], Ilona WROŃSKA[1]
and Sanaa MAHDI-ORAIBI[1]

THE NUMBER OF *E. coli* AND *C. perfringens* BACTERIA IN POULTRY WASTE AND SUBSEQUENT PHASES OF COMPOSTING

LICZEBNOŚĆ BAKTERII *E. coli* I *C. perfringens* W ODPADACH DROBIARSKICH ORAZ KOLEJNYCH FAZACH ICH KOMPOSTOWANIA

Abstract: Rapidly growing commercial poultry production generates large amounts of waste. Waste that accumulates during the poultry slaughter process often remains unprocessed, becoming a serious threat to people's health and the natural environment. Poultry production waste constitutes problems odour threat and dangerous sanitary threat. The aim of this study was to determine the population size of *Escherichia coli* and *Clostridium perfringens* in poultry waste and in successive stages of waste composting. Research material consisted of raw feathers collected immediately after the slaughter, samples of biological sludge from the centrifuge, mixture of straw, feathers and lime and processed compost. Microbiological analyses were conducted with the use of spread plate count method and the substrate was used in accordance with research standards. The size of population of microorganisms in the samples analyzed corresponded to the waste processing stage and group of microbes. The presence of *C. perfringens* strains was ascertained in all samples, whereas *E. coli* strains were identified only in raw feathers and centrifuge sludge, being most numerous in unprocessed material. A reverse trend was observed in case of *C. perfringens* with the highest population density in centrifuge sludge and least density in raw feathers.

Keywords: *E. coli*, *C. perfringens*, poultry waste, composting

Introduction

Within the last years a continuous development of poultry industry has been observed, which causes the increase of produced wastes. It depends mostly on the size of the farms and the meat processing plants and the applied production technologies. According to the Regulation (EC) No 1069/2009 of the European Parliament and of the Council of October 21, 2009, which came into force on March 04, 2011, the wastes are included in category 3 as inedible and by-products from animals subject to slaughter in a slaughterhouse [1]. The poultry slaughter by-products may become a material hazardous for both the natural environment and human health. Next to the high number of organic components, the wastes are full of pathogenic microorganisms, mainly from intestines and parasites' eggs [2, 3]. In the processing plants bacteria hazardous to human health are observed, *ie Salmonella enteritidis*, *Listeria monocytogenes*, *Yersinia enterocolitica*, and pathogenic strains *E. coli* and *C. perfringens* [4-6]. Thus the wastes should immediately undergo the treatments stopping undesired changes and should be processed into environmentally safe products. However the management process of large amounts of such wastes is relatively difficult. Sharpening the restrictive regulations of the European Union concerning the usage of slaughter wastes as additions to feeds even increased the problem of the wastes

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management [7, 8]. Thus it is so important to improve the existing methods of rendering the wastes harmless, as well as searching for and implementing new methods [9]. The most efficient methods of the slaughter wastes utilization include composting [10]. Compliance with appropriate treatment criteria may significantly force the pace of processing the wastes into non-hazardous, harmless and useful products as well as significantly reduce the processing costs [11-13]. Properly conducted the composting process can reduce the number of pathogenic microorganisms in poultry waste [14].

The conducted researches have been aimed at the determination of quantity of *E. coli* and *C. perfringens* in the poultry wastes and successive stages of the composting.

Materials and methods

The researches focused on the raw feathers from the poultry slaughter and the samples from the successive stages of their composting *ie* biological sludge from a centrifuge, mixture of straw, feathers and lime and the processed compost, received in the composting plant of a poultry processing plant (Fig. 1). The samples have been subject to a series of dilutions that have been used to perform microbiological inoculation on selective media, with the use of plate method. The scope of the conducted researches included determination of the quantity of: *E. coli* on a ready ENDO Agar medium (Scharlau company) and *C. perfringens* on Wilson-Blair medium used for the cultivation of anaerobic spore bacteria, reducing sulphates. The cultures were incubated in the temperature of 37°C for 48 hours. The quantity of the microorganisms has been provided in colony forming units (cfu) to 1 gramme of fresh samples mass.

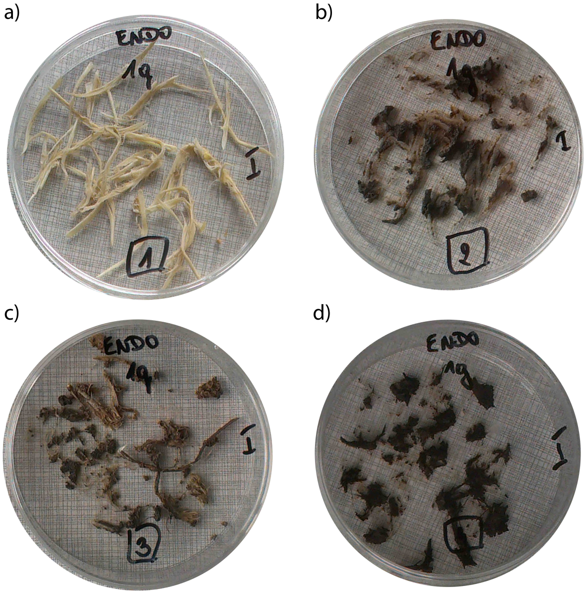

Fig. 1. The research material: a) raw feathers, b) biological sludge from the centrifuge, c) mixture of straw, feathers and lime, d) processed compost

Results and discussion

The conducted microbiological analysis of the researched samples revealed varied quantity of *E. coli* and *C. perfringens* bacteria. It has been proved that *E. coli* bacteria were the most numerous in raw feathers before the processing (Fig. 2). Their quantity was 240 cfu · g^{-1} of fresh mass and there were more of them (60%) than in the sludge from the centrifuge.

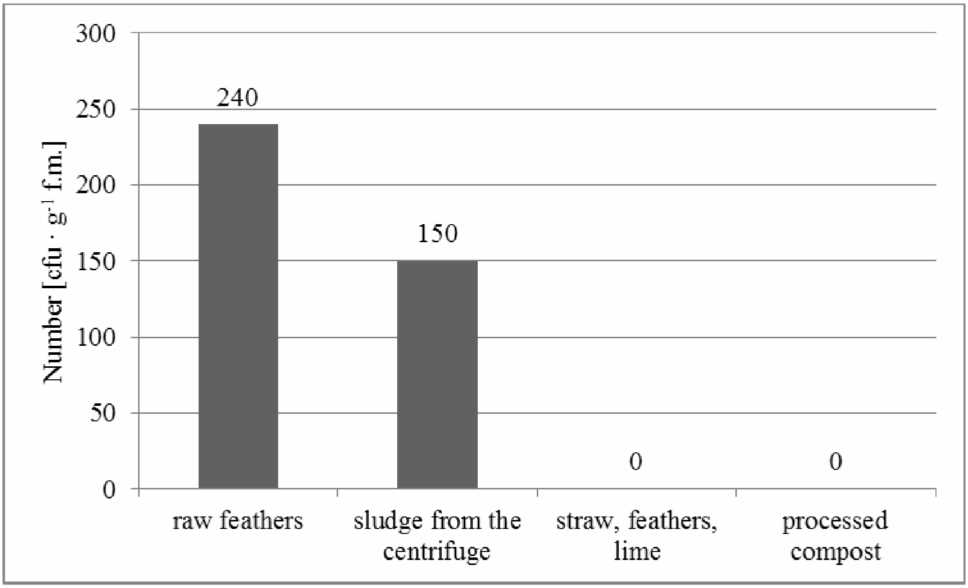

Fig. 2. The number of *E. coli* in research materials

The remaining samples *ie* the mixture of straw, feathers and the processed compost were free from this bacterium species. It has been stated that all the researched samples have complied with the standards binding in the regulation of the Minister of Agriculture and Rural Development for organic fertilizers, according to which the number of bacteria from *Enterobacteriaceae* family, specified on the basis of the number of aerobic bacteria, should be smaller than 1,000 colony forming units (cfu) per a gramme of the fertilizer [15]. The received results prove decreased number, or even elimination of *E. coli* bacteria in the successive stages of composting. The sterilization treatment has completely eliminated *E. coli* bacteria from the mixture of straw, lime and feathers. The conditions present in the composting container make it impossible for the bacteria to restore its numbers in the compost. This is proved in the researches of Wolna-Maruwka and her colleagues [16], who have stated that after 42.5 hours of the composting process the process of *Enterobacteriaceae* cultivation decreased in all the composted materials, which happened due to the increase of the temperature observed in the thermophilic stage. The same conclusions have been formed by Hassen et al [17]. According to Epstein [18] the number of *E. coli* and *Enterococcus faecalis* is reduced in temperatures 55-65°C. The author states that in such conditions the final material is free from pathogens after 14 days of composting. Chandna et al [19] and Singh et al [20] have also stated that the survival rate of the pathogens in the composted material depends on the content of the moisture, C/N ratio, pH, etc.

The analysis of the results of *C. perfringens* bacteria quantity, presented in the chart (Fig. 3), reveals their presence in all the analyzed samples. They were distinctly more numerous in the sludge from the centrifuge with the quantity of 520 cfu · g^{-1} of fresh mass. The lowest number was observed in the feathers prior to processing 5 cfu · g^{-1} of fresh mass.

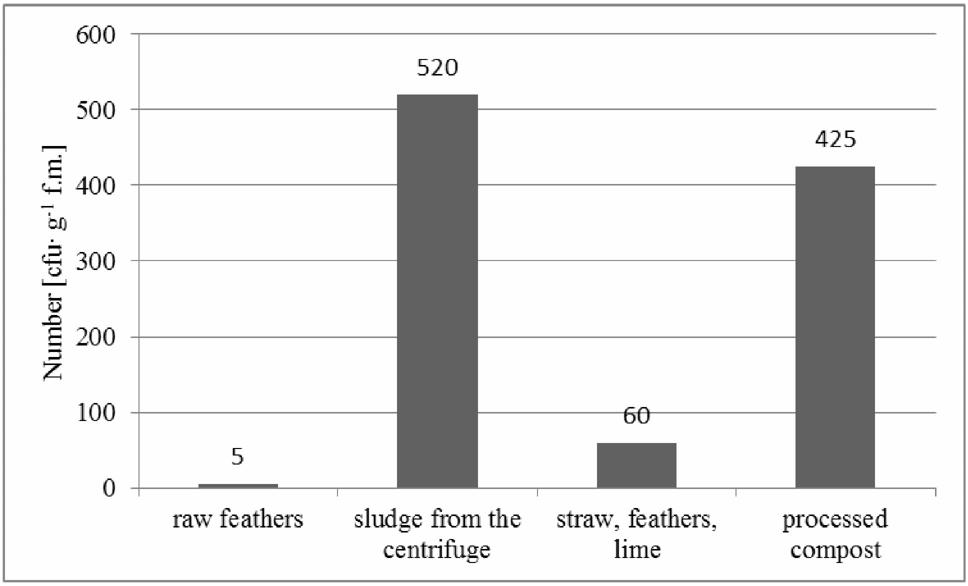

Fig. 3. The number of *C. perfringens* in research materials

In the next stage of composting the poultry waste, which was the mixture of feathers, straw and lime, a decrease of *C. perfringens* quantity was observed by about 88% in comparison to the quantity observed in the sludge from the centrifuge. The application of lime for the sterilization purposes could result in the decreased pathogen development, which is confirmed by numerous authors [21, 22]. The same phenomenon was also observed in relation to *E. coli*. However the ability of *C. perfringens* to form spores enabled them to multiply when the thermophilic conditions stopped, which was observed in case of the processed compost (425 cfu · g^{-1} of fresh mass). According to Payment [23] *C. perfringens* belongs to mesophilic microorganisms, extremely resistant to the environment changes and especially to the changes of temperature. Moreover, the researches of Raju et al [24] reveal that the spores of *C. perfringens* are able to survive in the temperature of 100°C for over 90 minutes. The specific properties of the species enabled recultivation of the bacteria after the sterilization.

Conclusions

1. The presence of *C. perfringens* bacteria was observed in all the samples, whereas *E. coli* bacteria were only observed in raw feathers and the sludge from the centrifuge. Their number depended on the stage of waste processing.
2. *E. coli* bacteria were the most numerous in the processed material, and *C. perfringens* in the sludge from the centrifuge.
3. During the advancing composting process a significant decrease of the quantity of the temperature sensitive *E. coli* bacteria was observed. While the quantity of *C. perfringens* bacteria was increased in individual stages of waste processing and in the compost.

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LICZEBNOŚĆ BAKTERII *E. coli* I *C. perfringens* W ODPADACH DROBIARSKICH ORAZ KOLEJNYCH FAZACH ICH KOMPOSTOWANIA

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Abstrakt: Intensywnie rozwijająca się produkcja drobiarska wiąże się z generowaniem dużej ilości odpadów. Powstające produkty uboczne podczas uboju pozostawione w stanie surowym stają się poważnym zagrożeniem dla środowiska naturalnego i zdrowia ludzi. Mogą stwarzać problemy odorotwórcze oraz istotnie groźne zanieczyszczenie sanitarne. Celem przeprowadzonych badań było określenie liczebności *E. coli* i *C. perfringens* w odpadach drobiarskich oraz kolejnych etapach ich kompostowania. Materiał badawczy stanowiły świeże pióra bezpośrednio po uboju, osad biologiczny z wirówki, mieszanina słomy, pierza i wapna oraz kompost przerobiony. Analizy mikrobiologiczne wykonano metodą płytkową, wykorzystując wybiórcze podłoża zgodne z normami. Liczebność mikroorganizmów w badanych próbach zależała od fazy przerobu odpadu i analizowanej grupy drobnoustrojów. Obecność bakterii *C. perfringens* stwierdzono we wszystkich próbach, natomiast bakterie *E. coli* tylko w piórach surowych i osadzie z wirówki, przy czym najliczniej występowały w materiale nieprzetworzonym. Odwrotną tendencję zaobserwowano w przypadku *C. perfringens*, które najliczniej zasiedlały osad z wirówki, natomiast ich mniejszą liczebność stwierdzono w piórach surowych.

Słowa kluczowe: *E. coli*, *C. perfringens*, odpady drobiarskie, kompostowanie

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COMPOSITE BASED ON FOAM LIME MORTAR WITH FLAX FIBERS FOR USE IN THE BUILDING INDUSTRY

KOMPOZYT NA BAZIE SPIENIONEJ ZAPRAWY WAPIENNEJ Z WŁÓKNAMI LNIANYMI DO ZASTOSOWANIA W BUDOWNICTWIE

Abstract: Building industry as an important branch of the economy of each country consumes significant amounts of energy and emits greenhouse gases into the environment (CO_2). These negative effects which affect on the environment have a contribution to make many of the restrictions recorded in the documents of sustainable development in the construction industry. The most significant are: environmentally friendly building products, energy efficiency of buildings, organized management of construction wastes including demolition materials. These considerations lead to the exploration and initiation of new construction materials and technologies, and in the final stage for the implementation of low-energy and passive buildings. This paper presents the results of preliminary studies of new composite material based on foam lime mortar, packed with natural flax fibers and additives and admixtures. The paper presents the physico-mechanical characteristics of the composite (strength parameters, absorption, coefficient of thermal conductivity, etc.) of different composition mix output. It is expected that the composite will be applied in the implementation of low-energy and passive building as parts fulfilling the structural and insulation function. The proposed material solution from natural ingredients meets the requirements of sustainable development in the construction industry. Studies are carried out under a cross-border grant from the Technical University in Brest and the material as the original solution is submitted to the Polish Patent Office.

Keywords: flax, organic fibers, lime binder, sustainable development

Introduction

Although ecological building is a relatively new phenomenon, it is growing rapidly in the construction sector. For this reason, natural, eco-friendly materials are still being sought since they are recyclable and can also be used in the construction industry as a construction material. In addition, and at the same time fulfilling the function of thermal insulation in accordance with the specifications of the heat transfer coefficient [1, 2].

In France and the United Kingdom, a study was carried out on a composite consisting of cut pieces of hemp stalks and lime binder [3, 4]. In Slovakia, in turn, a composite containing hemp was tested, for thermal loads effects on the mechanical properties [5-7]. In Brazil sisal fiber was added to concrete blocks [8]. Linen products (oil, straw) are widely used in construction industry, for example in the manufacture of flaxboards, linoleum, flax-seed oil [9].

The purpose of this article is to present a proposal for a composite material with a natural composition with flax applied to the low buildings, and to develop proposals of technological solutions. The material was tested for physico-mechanical and thermal properties, test results and analysis are presented in the further part of the article.

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Own research and used materials

The laboratory tests included the execution of composites based on lime binder involving fiber and straw from flax. The material properties were modified by adding additives and admixtures. Processing flax (containing straw and fiber inside) consisted of cutting it into lengths of about 25 mm. The diameter of flax straw was about 1-1.5 mm. A flax fiber itself was also used which was sliced into three fractions, the length of 10, 15 and 20 mm. In order to reduce the absorption of straw hydrophobization, natural impregnation (flax-seed oil) was applied.

Furthermore, hydrated lime and in some cases, lime with the addition of Portland cement CEM I 42,5R were used as a binder.

The aggregates used in small quantities include sand fraction of 0-1 mm and powdered limestone. In order to accelerate the binding of the lime binder, a pozzolanic admixture in the form of microsilica (Woerosil U-P) was applied to the mixture. Another admixtures include sodium bicarbonate ($NaHCO_3$) and citric acid ($C_6H_8O_7$). These compounds react together in the presence of water, which results in the emission of large amounts of carbon dioxide that accelerates the carbonation of lime.

In order to improve the thermal properties of the final product, composites containing foam, which was obtained by the mechanical mixing foaming agent with water, were also made.

Table 1

The components included in the various composites

	Water	Lime	Cement	Sand	Lime powder	Microsilica	Flax straw	Flax fiber	Foam
K1	X	X	-	X	-	-	X	-	-
K2	X	X	-	X	-	X	X	-	-
K3	X	X	X	X	-	-	X	-	X
K4	X	X	X	X	X	X	X	X	X

Four composites, differing in composition, were executed (K1, K2, K3, K4) (Table 1). In the composites K1 and K2, flax straw was impregnated by using flax-seed oil, while in the others, flax components did not hydrophobize. In the case of K3 and K4, cement was used in the amount of 30 and 25% by volume of the lime. The quantity of pozzolanic admixture was 5% by the weight of lime.

After mixing all components, samples were formed by light, hand-held tamping successive layers. After disassembling samples that maturated at air-dry conditions, tests on physical-mechanical and thermal properties of K1 and K2 composites were held after 90 days of maturation, and of K3 and K4 after 28 days.

The basic physical and mechanical properties of the material, such as bulk density, tightness, porosity, water absorption and compressive strength, were examined. All the tests were performed on cubic samples with the dimension of 10x10x10 cm. Thermal conductivity coefficient was measured on the basis of thermal parameters in Heat Flow Meter (HFM) instrument, on samples having the dimension of 25x25x5 cm. For each test, an outcome was defined as the arithmetic mean of the three samples. In order to evaluate the microstructure of the composite, a material was viewed by using a Scanning Electron Microscope (SEM).

Analysis of the results

Results of physical parameters are shown in Table 2. Bulk density values of composites are in the range from 0.44 to 1.29 kg/m^3, with the lowest values obtained by K3 and K4. This is caused by the presence of foam in the mixture, whose application minimizes the use of other ingredients.

Table 2

Examples of the physical properties of tested composites

Property	K1	K2	K3	K4
Bulk density [kg/dm^3]	1.29	1.05	0.5	0.44
Tightness [%]	50.5	48.3	23.0	17.5
Porosity [%]	49.5	51.7	77.0	82.5
Mass absorption [%]	28.0	39.0	67.0	77.0

K3 and K4 composites obtained higher porosity of about 60% in comparison with K1 and K2. The differences in these values are due to the foam used in K3 and K4 which forms a structure of closed pores filled with air.

Composites, as a result of relatively high porosity in the case of conventional building materials (such as concrete, brick), and the presence of straw and flax fibersshow absorption of 35% for K1 and K2, and 70% for K3 and K4. It was found that the hydrophobization of flax straw (K1 and K2) accelerates the process of lime binding in relation to samples in which impregnation was not applied (K3 and K4).

Strength tests showed that the compressive strength changed in the range from 0.45 to 0.65 MPa (Fig. 1).

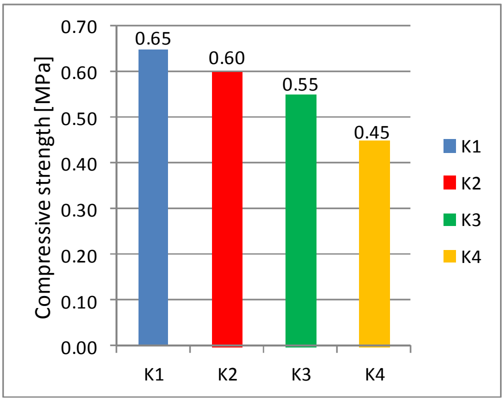

Fig. 1. The compressive strength of test samples

The analysis of the results allowed to observe the relationship of the strength of the material and density. If composite K1 obtains the highest strength which is also characterized by the highest bulk density, the quantity of the sand is also the highest compared with other composites. More importantly, the lowest strength and density reached K4, in which foam was applied. A percentage difference in strength between K1 and K4 is about 30%. Composite K4 has approximately three times lower bulk density than K1. It was concluded that by adjusting the composition of the mixture, strength properties of a composite can be increased, simultaneously trying to reduce the density of the material.

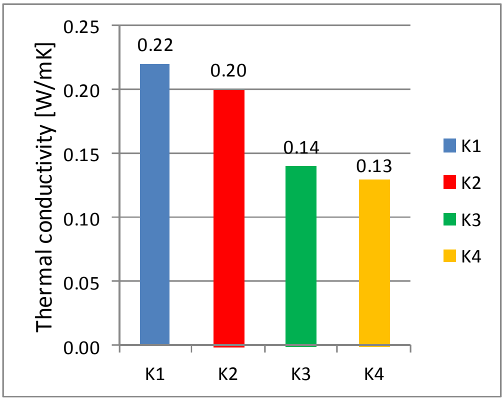

Fig. 2. The thermal conductivity of composites

Measured values of λ coefficient of tested composites are shown in Figure 2. Composite K3 and K4, despite lower content of fiber and straw in the volume of material in comparison with K1 and K2, showed higher thermal resistance due to the large amount of air voids that resulted from the application of foam. The λ coefficient for K3 and K4 amounted respectively to 0.14 and 0.13 W/mK. Composites K1 and K2, although having the highest bulk density, the thermal conductivity is relatively low (about 0.2 W/mK). It was noted that the increase of the amount of straw and flax fibers and the use of foam result in lowering of the thermal conductivity coefficient.

In Figures 3 and 4 the fiber and the structure of mortar K3 composite were shown respectively with the use of a SEM.

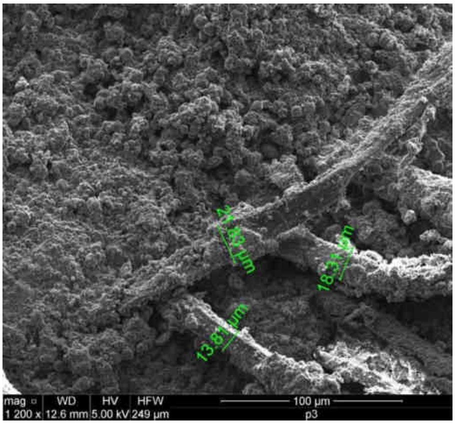

Fig. 3. Flax fiber

On the basis of the material structure analysis, it was observed that there occurred very good adhesion of flax fibers into the lime-cement matrix, which was consequent upon the rough surface of a fiber. In addition, in comparison with steel fibers used in conventional structural reinforced concrete, flax fibers exhibit high plasticity. This property is beneficial for the cohesion of material, which is due to better “matching” flax micro-reinforcement to the discontinuity of the composite structure, as opposed to steel fibers. Figure 4 shows the porous nature of the material and the calcium carbonate crystals in surroundings of partially hydrated cement grains.

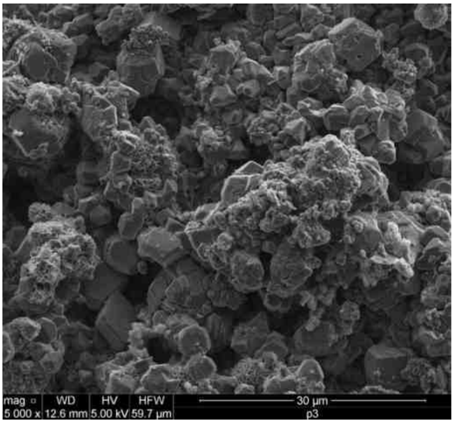

Fig. 4. The structure of mortar with foaming component

Possible applications of composites

The target application of the composite is the construction of walls. The components in the form of blocks, fill timber frame (Fig. 5) and monolithic wall (Fig. 6) are taken into consideration. As described in the previous section, the lowest obtained value of thermal conductivity was 0.13 W/mK. Table 3 presents the achievable U-values for a wall in different configurations of insulation and composite thicknesses.

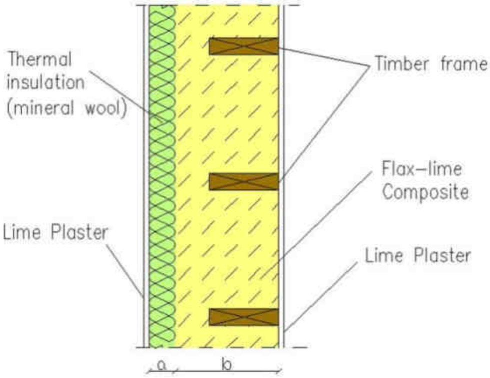

Fig. 5. Frame construction filled with the flax-lime composite and insulated with mineral wool

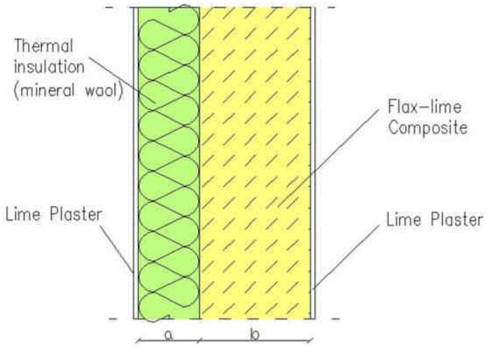

Fig. 6. Monolithic wall made of the flax-lime composite and insulated with mineral wool

Results 1-4 in Table 3 are related to the thermal requirements of the walls of conventional buildings, where the U-value ≤ 0.3 W/m^{2}K. Options 5-8 are intended for a passive and low-energy construction, where the required heat transfer coefficient is 0.15 W/m^{2}K, while recommended amounts to U ≤ 0.10 W/m^{2}K.

Table 3

Configurations of wall layers thickness and the corresponding value of "*U*" (alternative solutions)

Option	**a) Mineral wool**	**b) Flax-lime composite**	**U-value**
	λ = 0.042 W/mK	**λ = 0.13 W/mK**	**[W/m^{2}K]**
1	10 cm	20 cm	0.26
2	8 cm	30 cm	0.24
3	5 cm	40 cm	0.23
4	-	45 cm	0.29
5	20 cm	40 cm	0.13
6	20 cm	45 cm	0.12
7	25 cm	40 cm	0.11
8	30 cm	40 cm	0.10

Conclusions

The pilot study demonstrated the applicability of flax of composites. This natural ingredient can be the future of green building in Poland. The binder is mostly a natural product - which is lime. It is planned to reduce gradually the amount of cement to the zero level in the composite to increase the ecological nature of the product. This material is completely biodegradable and after demolition it can be used again for building. Also the foam-forming component is made of a blend of natural ingredients, harmless to humans and the environment; in contrast to the aluminium powder and the process of autoclaving in the case of aerated concrete.

Studies continue to search for the most optimal formula which gives the best strength and thermal results, according to the principles of sustainable development in the construction industry. The pilot study is simultaneously carried out, with the possible uses of additives that significantly accelerate the binding process of lime binder, which results in a rapid increase of strength of the material.

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KOMPOZYT NA BAZIE SPIENIONEJ ZAPRAWY WAPIENNEJ Z WŁÓKNAMI LNIANYMI DO ZASTOSOWANIA W BUDOWNICTWIE

Wydział Budownictwa i Architektury, Politechnika Lubelska

Abstrakt: Budownictwo jako ważna gałąź gospodarki każdego kraju zużywa znaczące ilości energii i emituje do otoczenia gazy cieplarniane (CO_2). Te negatywne skutki wpływające na środowisko były przyczynkiem do wprowadzenia wielu ograniczeń zapisanych w dokumentach zrównoważonego rozwoju w budownictwie. Do najważniejszych można zaliczyć: wyroby budowlane przyjazne środowisku, efektywność energetyczna obiektów budowlanych, zorganizowane zarządzanie odpadami budowlanymi, w tym rozbiórkowymi. Powyższe uwarunkowania prowadzą do poszukiwania i wprowadzania nowych rozwiązań materiałowych i technologicznych, a w końcowym etapie do realizacji budynków niskoenergetycznych i pasywnych. W artykule przedstawiono wyniki badań pilotażowych nowego materiału kompozytowego opracowanego na bazie spienionej zaprawy wapiennej, z wypełnieniem naturalnych włókien lnianych oraz z dodatkami i domieszkami. W opracowaniu przedstawiono cechy fizykomechaniczne kompozytu (wytrzymałość, nasiąkliwość, współczynnik przewodzenia ciepła itd.) o różnym składzie mieszanki wyjściowej. Przewiduje się, że kompozyt będzie miał zastosowanie przy realizacji budynków niskoenergetycznych i pasywnych jako elementy spełniające funkcję konstrukcyjną i izolacyjną. Zaproponowane rozwiązanie materiałowe z naturalnych składników spełnia wymogi zrównoważonego rozwoju w budownictwie. Badania realizowane są w ramach grantu transgranicznego z Uniwersytetem Technicznym w Brześciu, a materiał jako oryginalne rozwiązanie zgłoszono do Urzędu Patentowego RP.

Słowa kluczowe: len, włókna organiczne, spoiwo wapienne, zrównoważony rozwój

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ANALYSIS OF PHYSICAL AND MECHANICAL PROPERTIES OF LIGHTWEIGHT AGGREGATE MODIFIED WITH SEWAGE SLUDGE

ANALIZA FIZYCZNO-MECHANICZNYCH WŁAŚCIWOŚCI KERAMZYTU MODYFIKOWANEGO OSADAMI ŚCIEKOWYMI

Abstract: In recent years an increasing activity of sewage sludge management strategy is observed. This is due to EU legislation in the field of environmental protection, which constrains depositing this kind of waste. Sewage sludge is an organic-mineral material separated during the wastewater treatment. Because of physico-mechanical properties of the sewage sludge and the threat it can pose to human health and the environment, it has to be carefully processed before it is ultimately disposed of. In practice, there exist two directions of treatment of sewage sludge: natural management, which is covered by strict legislation, and combustion, which has certain advantages and disadvantages. Due to the above-mentioned legislation and EU standards in the field of environment protection, the sewage sludge management has become a major economical, ecological and technical problem. Thus, it is necessary to search for new methods of its utilization, independent of the present solutions. One of the method of utilization of the sewage sludge is production of the lightweight aggregate as a swelling agent, which creates the porous structure of the ceramic material during sintering. This paper presents the study of the basic physical and mechanical properties of lightweight aggregate derived from sewage sludge and clay. The aggregate was obtain in the forming method and sintering in 1150°C. Evaluation of physical properties was conducted on the basis of parameters such as specific density, bulk and volumetric density, porosity, water absorption. Mechanical properties of the aggregate was determined on the basis of resistance to crushing, abrasion in the Los Angeles drum, and frost resistance. Moreover, the removal of heavy metals from the extracts of aggregates was determined. The obtained results show that the lightweight aggregate with addition of sewage sludge meets the basic requirements for materials used in construction.

Keywords: sewage sludge, LECA, physical and mechanical properties of lightweight aggregate

Introduction

Sewage sludge is organic and mineral matter extracted from sewage in the course of its treatment. Due to its physical-chemical properties and a threat that it may pose to human health and the environment it must be subjected to appropriate processing by means of which it is finally disposed of. Pursuant to the Regulation of the Minister of Environment of 27 September 2001 on waste (Journal of Laws No. 112, 1206 of 8.10.2001), sewage sludge belongs to a group of 19 as waste from installations and equipment used for management of waste from sewage treatment plants, drinking water treatment and water for industrial purposes. EU legal regulations on environmental protection limit the possibility to store sewage. Ever-increasing quality requirements limit its use in agriculture. Admissible amounts of chemicals that sewage sludge may contain, are strictly defined by the standards such as *eg* Directive on Urban Waste Water Treatment 91/271/EEC [1] and its amendment - Directive 98/15/EC, "Sewage Sludge Directive" - 86/278/EEC [2], the directive which limits the use of sewage sludge in agriculture - 91/692/EEC, Directive on waste -

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2008/98/EC). The most significant consequence of another Directive on waste disposal - 99/31/EC [3] and the Minister of Economy and Labour is a ban on storage of sewage sludge the combustion heat of which exceeds 6 MJ/kg d.m. which has been introduced since 1st January 2013. This parameter effectively limits the storage of raw sludge on the site other than a hazardous waste landfill. In practice, there are two ways of the final disposal of sewage sludge: natural development, which is subject to more and more rigorous law regulations and thermal utilization. One of the advantages of this method is a significant reduction in the volume of deposits after burning, no time limits in utilization and energy recycling. These technologies, however, have some drawbacks. These processes are complex and costly, and in the case of co-incineration of sludge with fuel may produce some problems in meeting the standards for flue gas emissions and technical conditions required for conducting the process correctly. Due to the above-mentioned legislation and standardization requirements of the EU in the field of environmental protection, sewage sludge management has become a major economic, environmental and technical concern.

There has been an increased activity observed with regard to sewage sludge management strategy over the last few years. One of the methods of using sewage sludge may be applying it in manufacture of lightweight aggregate [4-11].

Lightweight aggregate used in production of lightweight concrete is generally porous material, the water absorption of which is usually higher than that of normal aggregate, which has an effect on the microstructure of hardened cement paste and the interfacial zone. The interfacial zone has been considered the weakest zone in composite concrete in terms of mechanical strength and permeability to fluids [12].

Materials and test methods

Testing material for production of lightweight aggregate was sewage sludge taken from the municipal sewage treatment plant "Hajdow" in Lublin and clay from "Budy Mszczonowskie" bed. Sewage sludge was subjected to tests in order to determine chemical parameters. Sewage sludge samples were taken from the temporary storage site, and then dried to a constant weight at 110°C. Dried sludge was ground and then added to clay (90% by weight) in the amount of 10% by weight. The process of making the substance homogeneous consisted in mixing components with the corresponding portion of water until a plastic consistency has been achieved. Then the formed balls of 16 mm coarse fraction were dried to a state of air-dry and kept in a laboratory oven at 110°C for 2 h. Dried samples were placed in a chamber furnace and fired at 1150°C for 30 minutes. Aggregate obtained as a result thereof was tested in order to determine physical and mechanical characteristics according to the standards [13-18].

One used the micro scanning electron microscope (SEM) - FEG Quanta 200 to determine the form and morphology of major minerals and chemical composition in microprobe. It also allows for performing the analysis of chemical composition based on energy dispersive of X-ray (EDS by EDAX company). Samples for SEM tests were glued onto the carbon holder by means of carbon glue. Preparations were then sprayed in the vacuum coater with a carbon layer the thickness of which was about 50 nm.

X-ray phase analysis was carried out using X-ray diffraction powder method using X-ray diffractometer Philips X'Pert APD (Fig. 1) with a goniometer PW 3020 and a Cu lamp and a graphite monochromator. The scope of the analysis included 5-65 2θ angles. Treatment of the results was performed in Philips X'Pert software and ClayLab program ver. 1.0. Mineral phase identification was based on PCPDFWIN database ver. 1.30 formalized by JCPDS - ICDD.

Leachability of hazardous substances such as cadmium, chromium, copper, nickel, lead and zinc was determined on the basis of the standard [13], and concentrations of heavy metals by means of AAS method using a spectrophotometer.

Test results

Results of sewage sludge tests

Test results of sewage sludge from the sewage treatment plant “Hajdow” in Lublin indicate that moisture content of sludge is 80.43%, alkalinity - 750 mg $CaCO_3/dm^3$, pH - 7.68, LKT - 92 mg/dm^3, ChZT - 136423 mg O_2/dm^3, dry mass - 19.57%, loss on ignition - 60.65%, the residue on ignition - 39.35%, density - 0.795 g/cm^3. Test results of the presence of heavy metals in sewage sludge show a significant presence of zinc ions (1175 mg/kg d.m.) and copper ions (442 mg/kg d.m.). Chromium ions are present in an amount of 74 mg/kg d.m., nickel - 42 mg/kg d.m., lead - 25 mg/kg d.m., cadmium - 8 mg/kg d.m.

X-ray phase analysis

X-ray diffraction photograph of sample phase composition (clay and lightweight aggregate from clay + sewage sludge) shows angular positions and intensity of diffraction reflections (Figs. 1 and 2). Main mineral components of clay from “Budy Mszczonowskie” bed are clay minerals represented by illite, kaolinite, beidelite, which are accompanied by quartz in minor amounts. Crystalline phases were identified based on basic interplanar quantities d, which amounted to particular minerals as follows: for beidelite - 4.49 Å, for illite - 10.01 Å; for koalinite - 7.14 Å and quartz - 3.44; 4.26 Å.

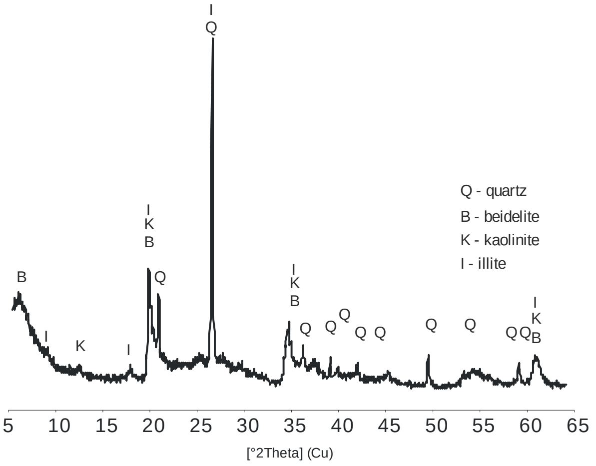

Fig. 1. X-ray diffraction photograph of clay from Mszczonow

It was found that in ceramic aggregate after firing at 1150°C there is mainly high temperature-type of quartz which is accompanied by mullite. As a result of heat treatment of sewage sludge there were also crystalline phases of hematite and graphite formed. Particular crystalline phases were identified through interplanar spacing: for quartz - 3.35 Å; 4.26 Å, for mullite - 5.40 Å, 3.40 Å, for hematite - 2.69 Å.

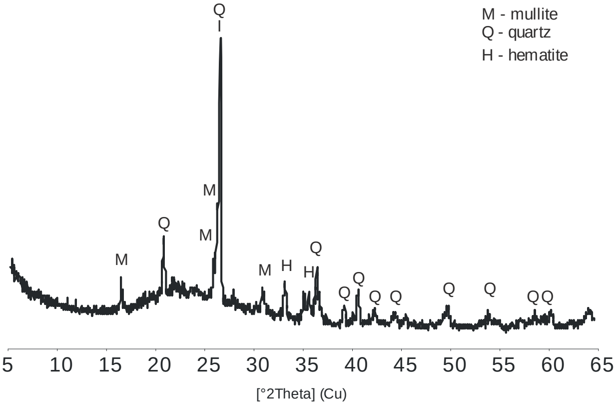

Fig. 2. X-ray diffraction photograph of mineral composition of lightweight aggregate fired at 1150°C

Scanning electron microscopy (*SEM*)

Lightweight aggregate is of porous structure and visible pores of spherical shape that are prevailing in the fired material are shown on Figures 3 and 4. The pore size varies and ranges from 2 μm to over 500 μm up to a few μm. Lightweight aggregate is characterized by compact and highly porous structure. Distribution of the pores is quite irregular.

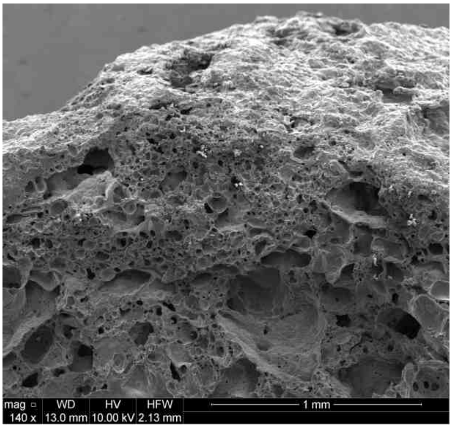

Fig. 3. Porous structure of lightweight aggregate fired at 1150°C, SEM above 140x

Fig. 4. Porous structure of lightweight aggregate fired at 1150°C, SEM above 8000x

Spectrum analysis of chemical composition of lightweight aggregate in a microprobe, fired at 1150°C (Figs. 5 and 6) indicates that predominant components are silicon, aluminum, iron. They are accompanied by potassium, calcium, magnesium. Chemical composition is as follows: SiO_2 - 53.6%; Fe_2O_3 - 9.33%; Al_2O_3 - 26.98%; K_2O - 5.58%; MgO - 2.15%; CaO - 2.36%.

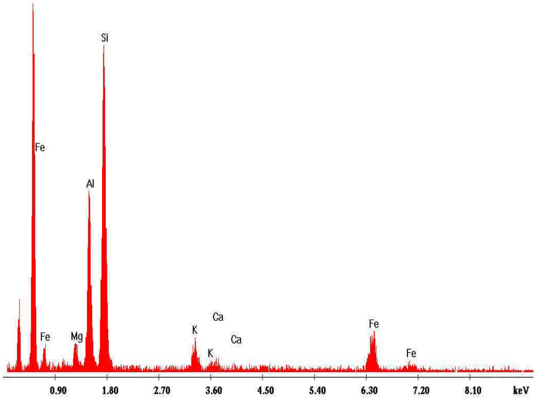

Fig. 5. Spectrum of chemical composition

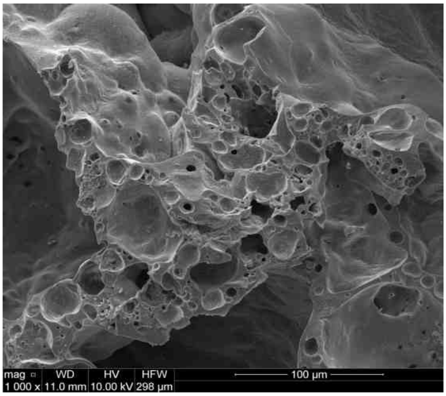

Fig. 6. Porous structure of lightweight aggregate fired at 1150°C, SEM above 8000x

Assessment of physical and mechanical properties of lightweight aggregate

Based on the results of the two samples taken and an arithmetic mean of their values, density was 2.59 g/cm^3. This is a typical value for this type of aggregate. Apparent density of lightweight aggregate subjected to tests was 0.812 g/cm^3, and bulk density was 0.414 g/cm^3. This value is close to the lower limit for bulk density of lightweight aggregate.

Absorptivity determined on the basis of the arithmetic average was 16.2%. Water wetted wall surfaces of lightweight aggregate which has been fired mainly on its surface, it did not go into the inside of the closed pores. After removing the material from water it regained its dry state fairly quickly. Compared to the acceptable limit for lightweight aggregate (< 37%) it is much lower. The porosity of aggregate subjected to test was 40%. The value of this parameter for the types of lightweight aggregate which are commonly manufactured at the market ranges from 20 to 50%. This value provides adequate absorptivity, high diffusivity of water vapour as well as thermal and acoustic insulation. The temperature of firing the aggregate plays an important role as far as the number of pores and their sizes are concerned. Void content or voids between grains is at the level of 52% due to the grain size of only (16 mm). The result obtained indicates that aggregate can be used in thermal insulation of roofs.

Frost-resistance of aggregate does not exceed 1%. The aggregate grain did not show any occurrence of cracks after the test. The aggregate is characterized by high porosity and large pore sizes. Water penetrating the grain probably has not filled in the whole surface of pores therefore it did not cause any damage to aggregate after freezing. Abrasion value obtained for the tested aggregate represents a high, unfavourable level. Such a large mass loss proves a very low resistance of aggregate to interaction of abrasive nature. Aggregate subjected to tests can be classified as LA80 as declared, therefore it cannot be used in road construction. Leachability measurements of chromium, cadmium, copper, nickel, lead and zinc in water extracts showed that the presence of metals is much smaller than it is tolerable (Table 1).

Table 1

Leaching of heavy metals from water extracts

Element	**Concentration in extracts [mg/dm^3]**	**Values admissible for aggregate [mg/dm^3]**
Cu(II)	0.015	< 0.5
Zn(II)	0.011	< 2.0
Cd(II)	0.001	< 0.02
Cr(II)	0.001	< 0.5
Ni(II)	0.036	< 0.5
Pb(II)	0.001	< 0.5

This means that you can use the tested aggregate as fully ecological building material of full value.

Conclusions

One obtained aggregate having good physical properties, of apparent density of 0.812 g/cm^3 and bulk density of 0.415 g/cm^3, absorptivity of 16.2%, porosity of 40%, void content of 52%, no coloring compounds. These results allow the use of lightweight aggregate modified with municipal sewage sludge for production of lightweight concrete. Appropriate porosity and void content also enable to use thereof to produce insulating concrete, and due to the lower water absorptivity and frost resistance compared to the standard lightweight aggregate, it should also be suitable as aggregate for concrete in moisture conditions. Considering many of the advantages, the lightweight aggregate obtained should be used in energy-saving building engineering, inter alia, in production of lightweight concrete, wall blocks, or as insulation for floors, ceilings.

The studies undertaken through developing the concept of lightweight energy-saving aggregate production from raw materials obtained from sewage sludge taken from sewage treatment plant aims at raising awareness of energy saving and environmental protection, as well as implementation of environment-friendly technologies in construction engineering.

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ANALIZA FIZYCZNO-MECHANICZNYCH WŁAŚCIWOŚCI KERAMZYTU MODYFIKOWANEGO OSADAMI ŚCIEKOWYMI

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Abstrakt: W ostatnich latach obserwuje się wzmożoną aktywność strategii zagospodarowania osadów ściekowych. Wynika to z przepisów prawnych UE w zakresie ochrony środowiska, które ograniczają możliwości ich składowania. Osady ściekowe są organiczno-mineralną materią wyodrębnioną ze ścieków w trakcie ich oczyszczania. Z uwagi na swoje właściwości fizykochemiczne oraz zagrożenie, jakie mogą stwarzać dla zdrowia ludzi i środowiska naturalnego, muszą być poddawane odpowiedniej przeróbce, za pomocą której są ostatecznie unieszkodliwiane. W praktyce istnieją dwa kierunki unieszkodliwiania osadów ściekowych: przyrodnicze zagospodarowanie, które objęte jest coraz większym rygorem przepisów prawnych, termiczna utylizacja, która ma zarówno zalety, jak i wady. Ze względu na wymienione powyżej prawodawstwo oraz standaryzację wymagań UE w dziedzinie ochrony środowiska zagospodarowanie osadów ściekowych stało się istotnym problemem ekonomicznym, ekologicznym oraz technicznym. Wzmaga to konieczność poszukiwania nowych, obok już istniejących rozwiązań, kierunków ich unieszkodliwiania. Jedną z metod wykorzystania osadów ściekowych może być zastosowanie ich do wytwarzania kruszywa lekkiego jako dodatku spęczniającego, który w warunkach wypalania prowadzi do utworzenia silnie porowatej tekstury spieku ceramicznego. Artykuł przedstawia badania podstawowych cech fizycznych oraz mechanicznych kruszywa lekkiego otrzymanego z osadów ściekowych i gliny. Kruszywo uzyskano metodą plastyczną przez wypalenie w temperaturze 1150°C. Oceny właściwości fizycznych dokonano na podstawie takich parametrów, jak gęstość właściwa, gęstość objętościowa i nasypowa, porowatość, nasiąkliwość. Cechy mechaniczne kruszywa określono na podstawie wytrzymałości na miażdżenie, ścieralności w bębnie Los Angeles, mrozoodporności. Dodatkowo określono wymywanie metali ciężkich w wyciągach z kruszyw. Badane właściwości wskazują, że otrzymane kruszywo keramzytowe z dodatkiem osadu ściekowego spełnia podstawowe wymagania stawiane materiałom stosowanym w budownictwie.

Słowa kluczowe: osady ściekowe, keramzyt, cechy fizyczne i mechaniczne kruszyw lekkich

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CHEMICAL COMPOSITION OF THE COMMERCE MINERAL WATERS VERSUS TAP WATER IN THE CITY OF KIELCE

PORÓWNANIE SKŁADU CHEMICZNEGO DOSTĘPNYCH W HANDLU WYBRANYCH WÓD MINERALNYCH ZE SKŁADEM WODY WODOCIĄGOWEJ MIASTA KIELCE

Abstract: Comparative analysis of the chemical composition of the commerce mineral and spring waters to tap water in the district city of Kielce has been presented in this paper. The research has been done using the latest analytical equipment which was stocked with ion chromatograph 883 Basic IC plus and spectrometer Optima 8000. The PHREEQC 2.17 program has been used in order to calculate the ion balances and *SI* index.

Keywords: mineral water, tap water, ion balance, *SI* index

Introduction

Recent observations show decrease in consumption of tap water and increase in consumption of the commerce mineral and spring water. Data obtained from the Nielsen agency show that over two billion litters of the mineral water (about 52 litters/person) worth over 2.2 billion PLN had been sold in Poland in 2008 [1].

So, in this paper we decided to answer the question: What do we drink?

In order to realise such a task ion compositions of the commerce mineral and spring water, described by the producers on the label of bottles, have been compared to these being the result of our investigation obtained using the latest analytical equipment. Additionally, the ion composition of tap water in the district city of Kielce has been determined.

The research has been done using the latest analytical equipment which among other things was stocked both with the ion chromatograph 883 Basic IC plus, produced by Metrohm company and the spectrometer Optima 8000, with excitation in plasma induced, produced by Perkin Elmer.

Ion composition of the analysed water

Three kinds of mineral water have been analysed in this paper. Low mineralized waters, such as: Kropla Beskidu, Zywiec Zdroj and Dobrowianka, with salts concentration ranged from 50 to 500 mg/dm^3; medium mineralized waters with salts concentration ranged from 500 to 1000 mg/dm^3, such as: Naleczowianka, Nestle Aquarel and Cisowianka and highly mineralized waters with salts concentration larger than 1500 mg/dm^3 such as: Staropolanka 2000, Muszynianka and Piwniczanka.

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The comparison of the results obtained in our investigation to the results declared by the producers of mineral waters is given in Table 1. The last row of Table 1 contains the results obtained for tap water in the city of Kielce.

Table 1

Comparison of the ion concentration values declared by the producers (P) to these obtained in our investigation (J)

Kind of mineral water	**Ion concentration [mg/dm^3]**									
	K		**Na**		**Mg**		**Ca**		**Cl$^-$**	
	P	**J**	**P**	**J**	**P**	**J**	**P**	**J**	**P**	**J**
Zywiec Zdroj	0	2.252	9.65	12.506	5.62	6.485	41.69	41.514	0	4.416
Kropla Beskidu	1	1.247	11.1	22.092	17.01	18.992	44.09	45.922	3.19	2.425
Dobrowianka	0	1.177	2	2.926	33.42	31.338	58.12	63.244	0	3.21
Naleczowianka	2.5	4.969	10	16.164	20	22.645	114.2	127.39	12.6	5.771
Nestle Aquarel	2.1	5.633	14	18.455	23.7	23.054	111.2	128.14	0	4.817
Cisowianka	2.5	4.242	11	14.798	21.9	25.362	130.3	141.04	2.5	1.5
Piwniczanka	13	9.971	133	116.6	87	82.79	180	213.6	0	11.28
Muszynianka	9	8.511	98	134.11	120	132.24	240	213.87	10	8.18
Staropolanka	52.3	46.249	128	145.66	59.8	55.6	309	335.7	2.9	7.844
Tap water	1.2	1.7387	10	15.883	8.53	9.241	90.19	86.275	27.9	21.943

The percent deviation of ion concentration values declared by the producers from these obtained in our investigation, larger than 20%, is specified in Table 2.

Table 2

Deviation of the ion concentration values declared by the producers larger than 20%
from these obtained in our investigation

Sort of mineral water	**Ion component**				
	K$^+$	**Na$^+$**	**Mg^{2+}**	**Ca^{2+}**	**Cl$^-$**
Zywiec Zdroj	100.00	22.84	-	-	100.00
Kropla Beskidu	20.00	49.76	-	-	31.55
Dobrowianka	100.00	31.65	-	-	100.00
Tap water	30.98	37.04	-	-	27.15
Naleczowianka	49.69	38.13	-	-	118.33
Nestle Aquarel	62.72	24.14	-	-	100.00
Cisowianka	41.07	25.67	-	-	66.66
Piwniczanka	30.38	-	-	-	100.00
Muszynianka	-	26.93	-	-	22.25
Staropolanka	30.98	-	-	-	63.00

Ion balance errors

Ion balance errors have been determined for all mineral and spring waters taking into account in our investigation including additionally tap water in the city of Kielce.

The Excel and PHREEQC 2.17 programs have been used in calculation above. Considering the fact that such ions as: HCO_3^-, SO_4^{2-}, Cl^-, Na^+, K^+, Ca^{2+} and Mg^{2+} constitute more than 90% and sometimes even 99% solubles in the underground waters only the ions mentioned above have been taken into account to obtain the ion balance [2, 4, 5].

According to the standard PN 89/C-04638/02 the permissible error of the ion balance is 5-10% if the sum of ions concentration in water ranges from 3 to 5 mval/dm^3. When such a sum ranges from 5 to 15 mval/dm^3 the acceptable error of the ion balance is 2-5% and finally for the ions sum larger than 15 mval/dm^3 the error of this balance should be less than 2% [3]. The above standard is very restricted and therefore in the paper [4, 6] it has been proposed that the determination of the ion composition in water is correct if the error of the ion balance is not larger than 10%.

Values of the ion balance errors obtained from the data given by the producers are presented in Figure 1. The ion balance errors received from the data obtained for the corresponding waters in our investigation are shown in Figure 2.

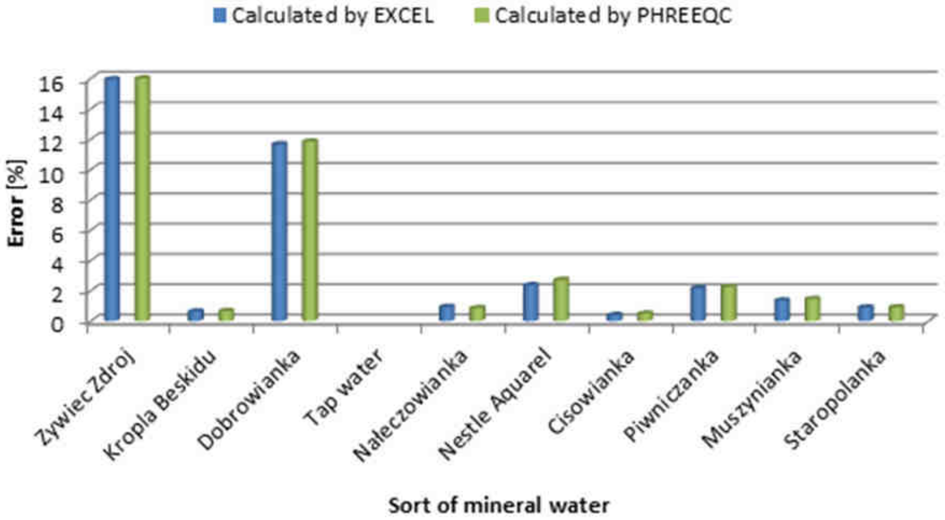

Fig. 1. Values of the ion balance errors obtained from the data given by the producers

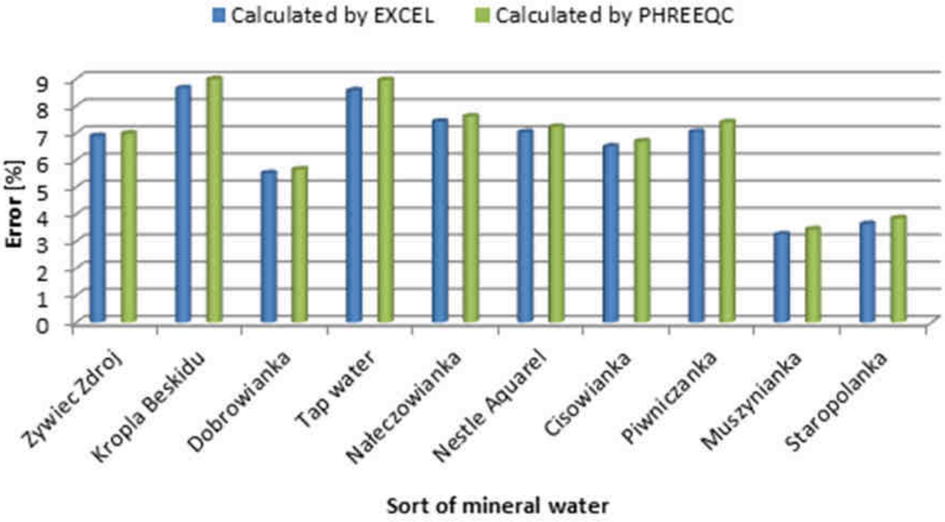

Fig. 2. Values of the ion balance errors received from the our data

Figure 1 shows that the values of the ion balance errors, obtained from the data placed on the labels of bottles, are less than 2% except of two waters: Zywiec Zdroj and Dobrowianka for these the ion balance error is larger than 10%. Such a high value of these errors is caused by the absence on the labels of the bottles concentrations of potassium, chlorine and sulfate ions.

The ion balance errors calculated from the data obtained in our investigation differ much more from these presented in Figure 1. The errors above 8% were obtained for tap water in the city of Kielce and for the mineral water Kropla Beskidu. The lowest results, a little below 3%, were received for the mineral waters like Muszynianka and Staropolanka 2000. The balance errors obtained for the other waters ranged from 5 to 7%.

A discerning analysis of the data placed on the label of the bottles by the producers shows the tendency to keep the ion balance errors below 2%. Of course, it might be caused by a very high accuracy of measurement of the ions concentration ordered by the producers but more probable it may be the attempt of such modelling of the ions composition of the mineral waters to fulfil the standard PN 89/C-04638/02.

Stability index (*SI*) of minerals in mineral water

Basing on the results of our investigation and using the program PHREEQC 2.17 one have determined the *SI* index for all waters being under consideration. From the theoretical point of view if for a given mineral its index $SI < 0$ then this mineral will dissolve in water, for $SI > 0$ the mineral will precipitate from water and finally if the $SI = 0$ the state of equilibrium between water and mineral is achieved. In practice however, due to the analytical errors, the state of equilibrium mineral-water is determined by the system of inequalities $-0.5 \leq SI \leq 0.5$, so solubility and precipitation of the minerals in/from water are described by the following inequalities:

$$SI < -0.5 \text{ and } SI > 0\text{, respectively}$$

Values of the index *SI*, obtained for the low mineralized waters and for tap water in the city of Kielce are presented in Table 3.

Table 3

Values of the index *SI* for the low mineralized waters

Mineral	**Kind of low mineralized water**			
	Kropla Beskidu	**Dobrowianka**	**Zywiec Zdroj**	**Tap water**
Anhydrite	–2.73	–2.56	–2.67	–2.13
Aragonite	–0.44	0.10	–0.28	–0.03
Calcite	–0.29	0.25	–0.13	0.12
Dolomite	–0.70	0.00	–0.18	–0.45
Gypsum	–2.50	–2.32	–2.44	–1.90
Halite	–7.50	–7.58	–7.60	–8.02

The data given in Table 3 show that all low mineralized water and tap water in the city of Kielce are stable with respect to aragonite and calcite. All these waters show a slight tendency to dissolve anhydrite and gypsum and a high ability to dissolve halite.

Values of the index *SI* obtained for the medium mineralized waters are given in Table 4.

Table 4

Values of the index *SI* for the medium mineralized water

Mineral	**Kind of medium mineralized water**		
	Naleczowianka	**Nestle Aquarel**	**Cisowianka**
Anhydrite	–2.86	–3.03	–3.58
Aragonite	0.08	0.50	0.26
Calcite	0.23	0.64	0.40
Dolomite	0.00	0.83	0.35
Gypsum	–2.68	–2.80	–3.34
Halite	–8.61	–8.63	–9.24

The data given in Table 4 show that all medium mineralized waters are stable with respect to aragonite. The high tendency to dissolve halite and slightly lower to dissolve gypsum and anhydrite characterise all these waters. Stability with respect to calcite and dolomite shows Cisowianka but Nestle Aquarel shows a little tendency to precipitates these minerals from water. Values of the index *SI* obtained for the highly mineralized waters are shown in Table 5.

Table 5

Values of the index *SI* for the highly mineralized waters

Mineral	**Kind of highly mineralized waters**		
	Piwniczanka	**Staropolanka**	**Muszynianka**
Anhydrite	–2.73	–2.56	–2.67
Aragonite	–0.44	0.10	–0.28
Calcite	–0.29	0.25	–0.13
Dolomite	–0.70	0.00	–0.18
Gypsum	–2.50	–2.32	–2.44
Halite	–7.50	–7.58	–7.60

The data given in Table 5 show that all highly mineralized waters are stable with respect to aragonite and calcite. A tendency to dissolve anhydrite, gypsum and halite show all these waters. The mineral water Muszynianka is stable with respect to dolomite.

Conclusions

Tap water in the city of Kielce characterises with a shortage of magnesium, calcium and acid carbonates ions. So, it cannot be used as a supplier of these elements to the water consumers. However such mineral waters like Muszynianka, Piwniczanka and Staropolanka 2000 may be used in this purpose. The mineral water Staropolanka 2000 characterises with the largest concentration of acid carbonates and calcium ions among the highly mineralized waters being considered in our investigation and may be treated as a supplier of these ions.

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PORÓWNANIE SKŁADU CHEMICZNEGO DOSTĘPNYCH W HANDLU WYBRANYCH WÓD MINERALNYCH ZE SKŁADEM WODY WODOCIĄGOWEJ MIASTA KIELCE

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Abstrakt: W pracy porównano skład chemiczny dostępnych w handlu wybranych wód mineralnych z wodą wodociągową miasta Kielce. Badaniami objęto wody mineralne niskomineralizowane: Kroplę Beskidu, Żywiec Zdrój i Dobrowiankę; średniomineralizowane: Nałęczowiankę, Nestle Aquarel i Cisowiankę oraz wysokomineralizowane: Staropolankę 2000, Muszyniankę i Piwniczankę. Oznaczenia wykonano, posługując się najnowocześniejszym sprzętem analitycznym, tj. chromatografem jonowym 883 Basic IC plus firmy Metrohm oraz spektrometrem emisyjnym ze wzbudzeniem, w indukowanej plaźmie, Optima 8000 firmy Perkin Elmer. Bilanse jonowe oraz wartość indeksów stabilności uzyskano, wykorzystując programy Exel oraz PHREEQC 2.17.

Słowa kluczowe: woda mineralna, woda wodociągowa, bilans jonowy, indeks stabilności *SI*

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PROCESSES OF SPREADING GAS POLLUTION ON HILLY FIELDS

PROCESY ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH NA OBSZARACH PAGÓRKOWATYCH

Abstract: A conditioning rank exists for the emission of a harmful substance, which overlaps in vicinity of varied ground-based objects. Consequently, part of the process of spreading pollution is determined by the flowing conditions and is shaped by their presence and distribution. However, under real conditions, complexes systems of terrain obstacles exist. A subject of interest among many authors is the flow and dispersion of pollutants surrounding single elements such as a hill or a building. This type of research enables a better understanding of the flow and propagation of pollutants on terrain with complex topography. The aim of the present work is the investigation of the influence of the complex character of a velocity field, particularly its periodic composition (non-stationary blowing) as well as rotating structures generated by obstacles such as hills on the propagation of various types of gaseous pollutants. The base of analysis represents the evolution of the carbon dioxide concentration in profiles surrounding hills or different locations in relation as well to the height of the source emission. By propagating a gaseous tracer in a rolling medium from a source located in a flush zone, a source's location relative to circulation zones of increased level turbulent fluctuations of flow velocity can be determined.

Keywords: experimental and numerical modeling, pollutants dispersion, gaseous pollutions, hilly field

Introduction

In many cases, the emission of harmful substances takes place in a neighborhood with various ground-based objects. As a consequence, a part of the dispersion process of pollution takes place in flow conditions formed by their presence and position. However, in complex systems and exist due to terrain conditions, a subject discussed by many authors is flow and pollution dispersion of small elements in a surrounding (hill, building) [1]. Such researchers are the first step to better understanding the flow and dispersion on terrain consisting of complex topographies. The tests of structured wind flow in mundane zones, which are comprised complex topographies, contribute series of information relevant for the most recent aerodynamics problems. Among other things, they relate to the dispersion of pollution, fire propagation, wind erosion and local condition researches which favor wind energetic. The last herein mentioned aspect forms the particular motive for wind flow analysis in the rolling medium. Flow features around single hills have both an influence conditions as inlet conditions and medium geometry. The collection of the mentioned factors can cause big differences in the kinematics within the jet stream which in general case sets detachment phenomenon, recirculation and adherence. The problem of wind flow over rolling media was taken in a series of work which involved both researches led in natural all-terrain condition, experimental modeling, and also numerical simulations. Most quoted work belong to Jackson and Hunt [2], presents analytical solutions for the genial hill shape, numerical Peterson models [3], Lenelin and

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[*] Contribution was presented during ECOpole'14 Conference, Jarnoltowek, 15-17.10.2014

others [2] and experimental results of Ferreira et al [4] and Kim et al [5, 6]. The focus of this research was mainly focused on deformation profiles of wind velocity flow according to apparition of symmetrical hills a low inclination [7, 8]. Geometry of media which was taken in most analyses does not appear to lead to strong detachment and recirculation zone. This constrains compliance of offered calculation methods [4] and experimental model consistency with a real wind field along the hill. Practical value of results of research denigrates the lack of information about general currents in nature, unfavorable aerodynamic modeled flow features. Detachment and recirculation cause strong fluctuations in velocity zones and change flow wind directions. Demodulation of these zones has an important meaning in wind engineering.

The testing bench

Scheme of measuring instrument is shown in Figure 1. The role of tap gas source, from the scoring source (pipe) from pointing source was played by carbon dioxide with a flow outlet velocity equal in approximation of undisturbed flow velocity, above layer zone.

To measure the concentration of CO_2 analyser Guardian plus was used. Analysed model of the hill was installed on a medium aerodynamic tunnel in the Aerodynamic Laboratory of Czestochowa University of Technology upon which the layer zone of thickness $\delta = 0.1$ m was generated, and profile velocity shape typical for an open ground with poor vegetation.

The velocity of the boundary of the layer zone amounted to $U_o = 13$ m/s. The shape of tested hill model is described by the relationship:

$$z_s = \frac{H}{2}\left\{1+\cos\left[\left(\frac{\pi}{2}\right)\left(\frac{x}{0.5W}\right)\right]\right\} \tag{1}$$

where: $H = 60$ mm, $W = 100$ mm (Fig. 1). Measurements were conducted for three different locations ($x = x_s$, $z = h_s$) and their emissions (Fig. 1), namely: (p1) $x_s = -W$, $h_s = 1H$; (p2) $x_s = 0$, $h_s = 1H$; (p3) $x_s = -W$, $h_s = 0$.

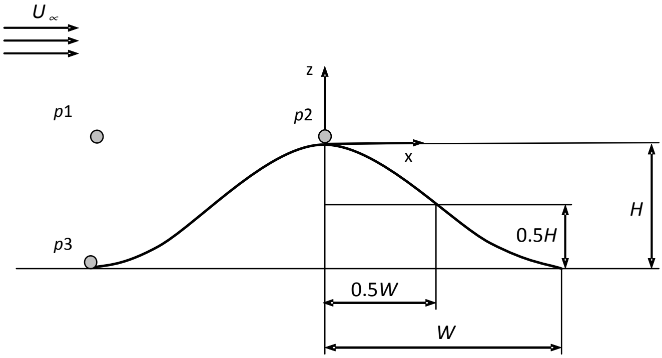

Fig. 1. Scheme of measuring testing bench with mounted researched object with marked location of emission CO_2 source

The measuring probe was mounted on a moveable support, which enables establishment of vertical concentration CO_2 profiles for chosen stream x = const set in localizations: $x = 0$; 0.6W; W; 2W; 3W; 4W. All measurements were done in a tunnel axis.

Work results

The aerodynamic outline of the researched object which enabled the detection of surrounding characteristic zones with strong diversified features, namely the area of increased velocity flow above the top of the hill and recirculation region of flow behind the hill (Fig. 2).

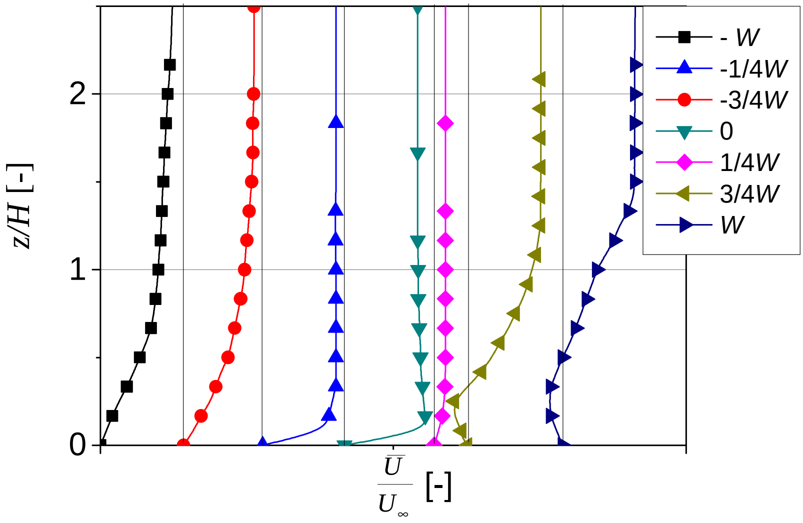

Fig. 2. View of evolution the average velocity profile component in flow around hill (scale: 0-1 for each profile)

The evolution of the concentration profile of carbon dioxide in a hilly environment for different locations and height source emissions is shown on Figure 3. As shown in the aforementioned diagram, courses differ on a particular drawing both qualitatively and quantitatively, but generally speaking, the presence of the terrain obstacle, which modifies the shape of emitted in environment trail of pollution in a relevant way could be ascertained.

This abides to features of velocity fields connected to an aerodynamic object in a fluid stream, but in a particularly closed environment in which recirculation zones arise from the zone of increased turbulence zone behind the hill. For the dispersion process of substances emitted from the source responsible are both mass diffusion mechanism, caused by concentration gradients and advection, transported pollution in a flow direction with help of average air flow and a turbulent transport process in which their own part has own turbulent velocity fluctuations. The maximum concentration values of carbon dioxide on the plume axis in every considered case varies.

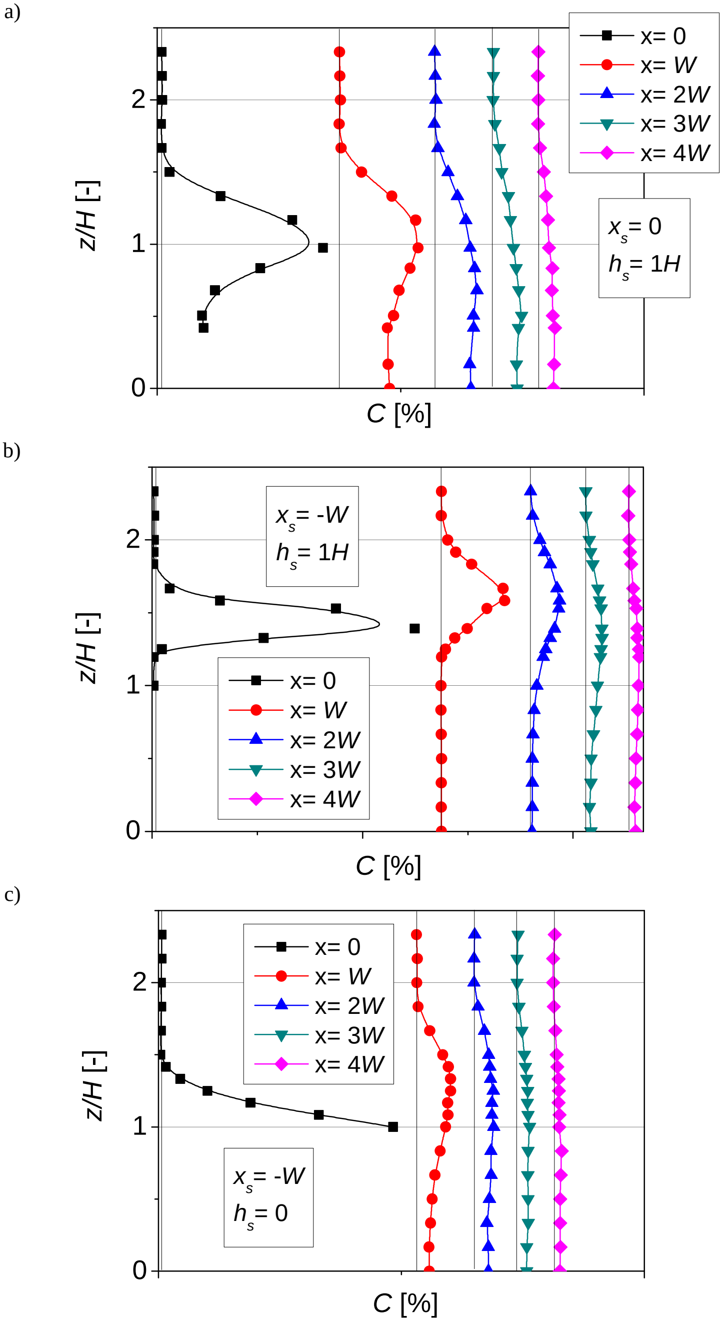

Fig. 3. View of concentration profiles of carbon dioxide in surroundings of a hill for a source emission in a locations: a) p1; b) p2; c) p3 (scale: 0-1 for each profile)

As the maximal values of distributions show qualitative similarity, they decreased with the distance from the source emission in every case, as long as the plume axis locations depend on a location at a predetermined distance from source location. As an effect of deflection of the stream which is emitted from a source in a location, (p2) ($x_s = 0$, $h_s = 1H$) an increased value of CO_2 concentration at ground level is obtained. In that case of the location of source the stream of carbon dioxide is provided almost directly into a recirculation zone behind the hill, where dilution and dispersion appears. The effect of that is mainly movement at ground level. In the case where the source was located on a height $h_s = 1H$ it was found in a distance W in front of the hill, then the dominant transport mechanism of emitted gas is advection, which causes the maxima of concentration to rise above the recirculation zone. At the same time the concentration of CO_2 is measured at ground level is practically equal to normal atmospheric values at close distances behind the hill. At long distances the influence of the situated source in terms of tab gas concentration at ground level disappears.

Summary and conclusions

To sum up obtained results, it can ascertained, that the dispersion of the CO_2 tab emitted from sources located in a flow flush on element of rolling medium and on its top performs in the different flow conditions, which are responsible for dissimilar character of course concentration of CO_2 in modeled wind field. Firstly, the source location in relation to the recirculation zone and the area of increased fluctuated turbulence velocity flow level is essential.

In the article, the initial results of researchers which suggest the significant influence of oscillation component of the velocity on pollution dispersion is shown. It is also acknowledged here that this theme still requires further research.

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PROCESY ROZPRZESTRZENIANIA SIĘ ZANIECZYSZCZEŃ GAZOWYCH NA OBSZARACH PAGÓRKOWATYCH

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Abstrakt: Istnieje szereg uwarunkowań, w których emisja szkodliwych substancji zachodzi w sąsiedztwie różnorodnych obiektów naziemnych. W konsekwencji część procesu rozprzestrzeniania się zanieczyszczeń przebiega w warunkach przepływowych kształtowanych ich obecnością i rozmieszczeniem. Mimo że w warunkach rzeczywistych występują złożone układy przeszkód terenowych, przedmiotem zainteresowania wielu autorów jest przepływ i dyspersja zanieczyszczeń w otoczeniu pojedynczych elementów, jak wzgórze czy budynek. Badania tego typu służą lepszemu zrozumieniu przepływu i rozprzestrzeniania zanieczyszczeń w terenach o złożonej topografii. Celem niniejszej pracy jest zbadanie wpływu złożonego charakteru pola prędkości, a szczególnie jego składowej okresowej (niestacjonarnych podmuchów wiatru) oraz struktur wirowych generowanych obecnością wzgórza na rozprzestrzenianie się różnego typu zanieczyszczeń gazowych. Podstawę analizy stanowi ewolucja profili koncentracji ditlenku węgla w otoczeniu wzgórza dla różnego położenia i wysokości źródła emisji. Na rozprzestrzenianie się znacznika gazowego emitowanego ze źródła usytuowanego w strefie napływu na faliste podłoże ma wpływ przede wszystkim położenie źródła względem strefy recyrkulacji oraz obszaru o podwyższonym poziomie turbulentnych fluktuacji prędkości przepływu.

Słowa kluczowe: modelowanie rozprzestrzeniania zanieczyszczeń, zanieczyszczenia gazowe, teren pagórkowaty

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Adam GNATOWSKI[1] and Renata GNATOWSKA[1]

QUALITY MANAGEMENT AND ANALYSIS METHODS OF PROCESSING PLASTICS RECYCLING IN POLYMER

ZARZĄDZANIE JAKOŚCIĄ I ANALIZA METOD RECYKLINGU W PRZETWÓRSTWIE TWORZYW POLIMEROWYCH

Abstract: The paper presents the method of recycling and quality management in the recycling process of polymeric materials. Recycling of mixed polymer materials is one of the most complex processes in manufacturing. It is important to be able to manufacture the materials of the secondary properties of an acceptable degree of mixed polymer waste. In this way have been eliminated long and costly separation processes. Properties of such materials are polymers which are disadvantageous because constitute them - mainly PE, PP, PS, PVC, PET etc. - are incompatible and form a multi-component system in which the individual phases do not exhibit significant adhesion. In addition, other materials present different types - paper, metals, dyes - act as contaminants and contribute to the further deterioration of mechanical properties. In almost all cases, the properties of the mixture are worse than the properties of the individual components. If you need to produce products that must meet high requirements for mechanical properties is not the possibility of using recycled material. They are used so other methods of recycling as raw materials and energy, including paralysis method, hydrocracking and gasification. Management quality now plays an increasingly important role in the recycling of plastics. The quality of the production becomes an important element of competition, which increasingly can decide the success of the recycling industries.

Keywords: recycling, polymeric materials, quality management

Introduction

Recycling involves reprocessing of substances or materials contained in waste, in the manufacturing process in order to obtain a substance or material for the original purpose or for other purposes. The aim of recycling is to:

- protection of natural resources - the use of recycled materials reduces the use of raw materials and shortage of stocks of natural resources,
- environment - raw material extraction and processing of consumer goods is a constant related to the load and environmental degradation; this means that the protection of natural resources is also the environmental,
- energy saving - are recyclable energy sources, their use leads to energy conservation as long as the energy input to the recovery is less than the energy that they entail, and which can be obtained through them. Saving energy is therefore also environmental protection.

The operating principle of recycling is to maximize the re-use of the same materials, including the minimization of expenditures to be processed, which are protected natural resources, which are used to produce them and the raw materials used for further processing.

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[*] Contribution was presented during ECOpole'14 Conference, Jarnoltowek, 15-17.10.2014

Recycling takes place in two areas: production of goods and the subsequent formation of these wastes. Assumptions recycling assume the forced attitudes goods manufacturers, favoring the production of the most recyclable and creating the appropriate behavior of the recipients of these goods.

Recycling is a system organization of circuit materials that can be repeatedly processed (Fig. 1).

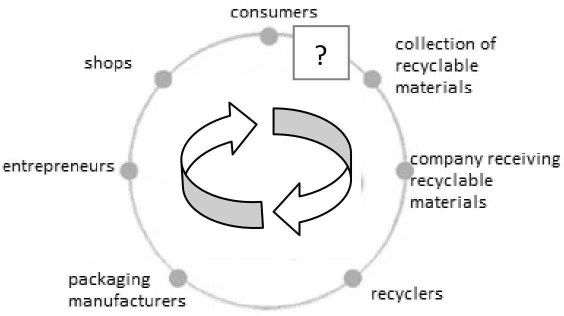

Fig. 1. Circuit materials in the environment

The system consists of the following elements:

- appropriate state legislative policy favoring recycling,
- waste treatment technology development, primarily in order to use most of their parts,
- designing goods with the widest possible use of these recyclable materials,
- design of homogeneous material and goods as possible, simplifying their subsequent dismantling and waste segregation,
- design property of a combination of different materials in such a way that the subsequent separation of the components consist of homogeneous materials could be easier,
- design goods in such a way to make the most of its components be suitable for re-use without treatment or with minimal to bring to a complete,
- system for determining both the product packaging and components of these products, in order to facilitate the recognition and segregation of waste,
- ecological education of society and to promote environmentally friendly behavior and organization,
- logistics sorting, collection and collection of used goods and their components,
- processing (previously prepared) of waste and the recovery of raw materials [1, 2].

Polymeric materials are characterized by a huge diversity in terms of chemical structure and composition and formulation. Therefore, recycling of polymeric materials has a number of limitations. A huge role in the recycling process plays a quality management. It determines the ratio of the recycling industries and its staff, for carrying out activities. In readable illustrates the quality policy objectives and the company's management, helps in the implementation of the quality management system.

All the planned and systematic and, if necessary, proven activities implemented within the quality system, are used to excite the sound of confidence as to the object (product, service) meet the quality requirements. There is always action to ensure the quality are properly organized. Quality management requires, document and maintain a quality system [3].

Documentation and quality assurance system

In the case of recycling companies, a very important element of the quality management system are documentation that confirms compliance of the recycling process.

The raw material in the manufacture of polymeric materials and any additives to be used as long as it can be reasonably justify. Production processes should also use renewable raw materials, avoid toxic substances.

In stark much better to prevent the formation of waste rather than dispose them. Quality assurance system implemented by the recycler must in an appropriate manner to ensure compliance with the requirements contained in permits for the processing of plastics in the recycling process. All the elements, requirements and provisions adopted by the recycler quality assurance system must be documented in a systematic manner and orderly manner in the form of written documents statements and procedures.

The quality system documents must permit a consistent interpretation of the quality policy and procedures such as quality programs, plans, manuals, records and measures to ensure traceability.

The documentation consists of the following elements:

- quality policy manual, containing a clear definition of quality goals of the recycler, the organization of the company, in particular the organizational structures, the responsibilities of the managerial staff and their organizational authority for plastics recycled;
- quality control plans, including plans for the characteristics of the raw material and plastic recycled, qualification of suppliers, sorting processes, washing, deep cleaning processes, processes or any other part of the process relevant for the quality of plastics recycled, including the identification of critical points quality control plastics recycled;
- management and operational procedures used to monitor and control the whole recycling process, including the inspection and quality assurance techniques at all stages of the manufacturing process, in particular the establishment of critical limits at critical points for quality plastics recycled;
- methods of monitoring the efficient operation of the quality system, in particular its ability for plastic production the recycling of appropriate quality, including checks of products satisfying the requirements;
- records of tests and analyzes or other scientific evidence applied before, during and after the production of plastics recycled, the frequency of testing and the test equipment used; in an appropriate range must be possible to trace back the calibration of the test equipment;
- recording documents adopted [4].

Key issues related to quality management in the recycling of plastics concern:

- Transport - special attention should be paid to the way of organizing collection system, the time between order receipt and acceptance of waste. It is also important if there is an agreement of carriers, ensuring sustainable transport, and what type of transport containers will be used.
- Raw materials - is of great importance is how much of the raw material is recovered, and how much of them goes to the landfill.
- Hazardous substances - it is necessary to know the different types of recipients of hazardous waste and to check whether they have a permit for disposal of hazardous substances.
- Environmental management system - is of great importance is whether the company has a recycling environmental policy and observes it, what are its environmental goals, and if it works on the basis of an environmental management system.
- Quality system - make sure the company has a policy of recycling and observes its quality and whether it operates in accordance with a certified quality management system [4].

By the quality of the materials by mechanical devices meant primarily getting better adapt the products to the requirements and expectations of customers.

The introduction of a quality management system will draw attention not only to control the quality of products, but also to monitor and correct operation of the quality management system, customer service personnel, identifying requirements for raw materials, standardization and statistical process control, enabling impact on the article already during its manufacture.

Methods for recycling of plastics

Currently in Poland, most going to landfill becoming better organized and secured. This natural degradation of waste is indeed the simplest method to eliminate them, but at least economically, socially, and unacceptably large spaces dedicated landfills. Also keep in mind that due to the need to fulfill the recommendations and EU directives such a solution becomes legally unacceptable for many categories of waste (including polymer). The only way to dispose of waste landfilled is to recover a small portion of the energy by collecting and burning biogas generated in landfills.

There may be hope of composting biodegradable plastics, the production and use is currently at a very low level.

Material recycling

Material recycling, is the repeated, direct processing of waste without the use of chemical processes. This method can be used both in the case of thermoplastics (polyolefins, polyamides, polystyrene, polycarbonate, polymethylmethacrylate, polyester) and thermosetting plastics (*eg* polyester and epoxy resins) [1, 5, 6].

Waste water treatment is the process to obtain the material for re-processing. This is the most rational way of polymeric waste as it allows reduction of the production of polymers original. This allows you to reduce the emission of harmful substances into the environment and energy necessary to produce new polymers. This method, however, is economically viable only for a certain group of polymers, and in the case of waste sorted well and uncontaminated [1, 5].

Methods belonging to this type allow for the recovery of recyclable waste plastics pure fractions nutritious polymers suitable for re-processing. The resulting product is called recycle, or regenerated regranulate. Properties of regranulate are generally worse than the material from which it was made [6]. Frequently regranulate is also 2-3 times more expensive than a new raw material (the cost of waste sorting, preparation for recycling and the same alteration). However, it is now quite common to use recycled material in the automotive industry.

In the next stages are prepared in connection with the deterioration of the properties of the recycled material getting "worse" elements, *eg* material of the bumpers is made into rugs (recycling or secondary two cyclic). Founded in Poland PRO PVC Consortium Initiative estimates that in the near future will evolve dynamically recycling material polyvinyl chloride (PVC), whose production from year to year increases, and PVC recyclate is very satisfactory properties. Unfortunately, because of the price and satisfactory property other recyclates in the world, only 7% of plastics can be recycled as material [5].

Feedstock recycling

Degradation of polymers into fractions of lower molecular weight in order to recover monomers (oligomers), the recycling of raw material (chemical), although potentially beneficial, is not only very expensive. Research on processes such as pyrolysis, hydrolysis and hydrogenation will perhaps in the future to build cost-effective, working on large-scale installations using waste plastic. This process focuses on plastics such as PET and polyurethanes [1, 5].

Recycling energy

The methods rely on the burning of plastics and conversion of chemical energy into heat or electricity or destructive conversion polymers of low molecular weight compounds in the pyrolysis process, hydrocracking or partial oxidation, used as a fuel or chemical feedstock. Utilizes the world in this way 16% of the waste plastics. The energy recycling involves hopes for processing the waste, which can not be described earlier methods such as recycling. Municipal waste, which are a mixture of very different materials highly contaminated. All these processes are carried out mostly in the refining plant and waste are in addition to conventional refinery feedstock (*eg* Heavier fractions of crude oil). Products are fuels, oils and raw materials of organic synthesis [5].

Pyrolysis

There are many methods for the pyrolysis of waste polymer materials. These include processes in the engine's gas-solid, liquid-solid, and the vacuum pyrolysis [7].

In previously known pyrolysis techniques used boilers, autoclaves, ovens, rotary screw systems and fluidized beds [7, 8]. The process is versatile and he can be subjected to plastic mixture after proper grinding without preliminary separation. Perm is the presence of PVC to 2%. If larger quantities hydrocarbon fractions contain traces of organochlorine compounds. The formation of these compounds can be avoided by the addition of calcium oxide to bind the hydrogen chloride evolved. The resulting calcium chloride causes movement problems, however, resulting from the lumps of solid fraction part of the fluidized. It is therefore better additive ammonia, which allows the binding of hydrogen chloride, ammonium chloride.

In the case where the pyrolysis of waste is located within the refinery, is already at capacity of 40 thousands Mg/year of economic indicators are very favorable [9].

Gasification

Gasification of waste plastics is partial oxidation therein at a temperature of the organic components 1350-1600°C under a pressure of 15 MPa. As the oxidizing agent, oxygen is used most often in admixture with steam.

The resulting gas (after removal of water and carbon dioxide) mainly composed of carbon monoxide and hydrogen, and the solid residue is elemental carbon and inorganic material gasified components (fillers, impurities). In the process without the formation of liquid products. In this process, however, should be taken into account specification of the processed materials (plasticity, degree) and the purpose of the resulting product gas (fuel gas, synthesis gas). The tested in a pilot-scale technical solutions are first waste heat plasticization (melted), preferably such. Mixture with pus or heavy residues and coal tar liquid introduced into the reactor. Gasification can be subjected to all kinds of waste plastics (both thermoplastic and thermosetting) and rubber [9].

Despite many objections, it is estimated that recycling of energy in the future will be the primary form of exploitation of waste plastics. It is anticipated that in Western Europe in the coming years will be processed 50% of plastic waste, especially those fractions which could not be profitably used in a different way [1].

Discussion

The design of the recycling process (Fig. 2) of different products, in addition to the ecological principles of production, should include all phases of the life of these products until after their removal and reprocessing according to the following scheme. This procedure is already beginning to be seen in the automotive industry, at which time the disassembly of any part or parts plays a very big role. Also implemented in the electronics industry many trials of new technologies, of the future of the recycling process. One example pro-recycling approach is the design and production of beverage bottles [9].

As shown by the experience of the many reasons you can not opt out of the packaging of polymeric. Transport for example. Beverages in packages of polymeric materials is cheaper than bottled. Reducing consumption of plastics can be achieved by the use wherever possible of reusable packaging, as well as by improving the properties of polymer materials, allowing for example. Material weight reduction necessary to obtain a product that meets users by limiting their use, re-processing of waste packaging and the use of biodegradable packaging [1].

Management quality now plays an increasingly important role in the recycling of plastics. The whole process includes:

- planning,
- organization,
- motivating,
- control,

all activities relating to the shape and maintaining its quality standards.

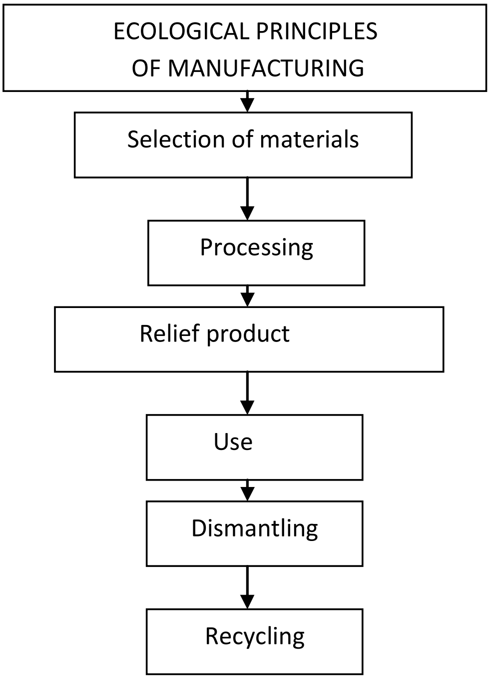

Fig. 2. Designing the recycling process [9]

Before the plant will proceed to the efforts to start recycling line is necessary to pay special attention to:

- used for the disposal of packaging waste technologies adapted to local conditions and take into account the available infrastructure, the number and range of waste, continuity of supply, as well as size of the market and its absorbency products from recycled materials,
- range of knowledge in the field of chemistry and physics,
- to enable better use of the waste material,
- knowledge of the basic characteristics of the material - it allows work on the modification of the properties of plastic waste to improve its quality. Proper selection of compositions - often contain additives specifically designed for recycling, fillers and modifiers,

- allows for the processing of secondary materials with high yield, good quality products at the same time,
- the market value of the waste - it results mainly from the evaluation of their quality - for a potential recipient is essential quality product which can be obtained from recycled material, and which can be difficult waste processing using standard methods of recycling.

Quality in manufacturing and services is becoming an important part of the competition, which increasingly can determine the success of the recycling industries. Quality management often treated as an action that leads to increased production costs. Improving quality involves the introduction of new technologies, production processes, more expensive materials. Bringing recycling company to the relevant standards is only possible by the improved quality of services and manufactured products.

Conclusions

The different ways of working of plastics recycling, resulting the benefits and limitations show that there is no one universal and optimal in terms of economic data strategy for dealing with waste management of plastics.

When selecting the optimal solution, depending on the type of material and extent of contamination, must take into account several different, non-exclusive solution.

Please be aware that recycling is a process that should be planned years in advance, paying particular attention to the quality management system.

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ZARZĄDZANIE JAKOŚCIĄ I ANALIZA METOD RECYKLINGU W PRZETWÓRSTWIE TWORZYW POLIMEROWYCH

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Abstrakt: W pracy przedstawiono metody recyklingu oraz możliwości zarządzania jakością w procesie recyklingu materiałów polimerowych. Recykling zużytych mieszanych tworzyw polimerowych jest jednym z bardziej skomplikowanych procesów w przetwórstwie. Istotna jest możliwość wytwarzania materiałów wtórnych o dających się zaakceptować właściwościach ze zużytych mieszanych polimerów. Wyeliminowane zostałyby w ten sposób długotrwałe i kosztowne procesy segregacji, które obecnie oparte są na wstępnej segregacji przez konsumenta oraz na następujących po niej ręcznych lub automatycznych procesach wykonywanych przez zakład odzyskujący tworzywa. Właściwości takich materiałów są niekorzystne, ponieważ polimery, które się na nie składają - głównie PE, PP, PS, PVC, PET itd. - są niekompatybilne i tworzą układ wieloskładnikowy, w którym poszczególne fazy nie wykazują znaczącej adhezji. Ponadto obecne inne materiały różnych typów - papier, metale, barwniki - działają jak zanieczyszczenia i przyczyniają się do dalszego pogorszenia właściwości mechanicznych. W prawie wszystkich przypadkach właściwości mieszaniny są gorsze od właściwości poszczególnych składników. W przypadku konieczności wytwarzania produktów, które muszą spełniać wysokie wymagania co do właściwości mechanicznych, nie ma wówczas możliwości zastosowania recyklingu materiałowego. Stosowane są więc też inne metody recyklingu, jak: surowcowa i energetyczna, w tym metoda pirolizy, hydrokrakingu i zgazowania. Zarządzanie jakością odgrywa obecnie coraz bardziej znaczącą rolę w procesie recyklingu tworzyw polimerowych. Jakość w produkcji staje się ważnym elementem konkurencji, który w dużym stopniu może decydować o sukcesie przedsiębiorstw zajmujących się recyklingiem.

Słowa kluczowe: recykling, materiały polimerowe, zarządzanie jakością

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Janina GOSPODAREK[1]

EFFECT OF SOIL POLLUTION WITH OIL DERIVATIVES ON THE OCCURRENCE OF ISOPODA

ODDZIAŁYWANIE ZANIECZYSZCZENIA GLEBY ROPOPOCHODNYMI NA WYSTĘPOWANIE ISOPODA

Abstract: The research aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of Isopoda occurrence. The following objects were established in two series (natural and supported bioremediation): control - unpolluted soil; soil polluted with petrol; soil polluted with diesel fuel and soil polluted with used engine oil (dose: 6000 mg of fuel · kg^{-1} d.m. of soil). Epigeal fauna was trapped using Barber's traps. During the periods from June to October 2010, from May to October 2011 and 2012 the traps were emptied once a week. Activity of Isopoda order representatives was reducing under the influence of soil pollution with engine oil - the result was discernible even after 14 months from the moment of contamination. Pollution with petrol generally did not affect the occurrence of Isopoda, whereas contamination with diesel oil even favoured their presence after two years from the contamination moment. Supported bioremediation applied to the soil contaminated with diesel and engine oils was regulating, *ie* contributed to increase in the number of trapped specimens in places where the oil derivatives limited their occurrence (the object polluted with engine oil) or to diminish their activity where the soil pollution favoured the occurrence of crustaceans (the object where the soil was contaminated with diesel oil in the 2012 season). In result, the number of trapped Isopoda was similar as in the unpolluted object.

Keywords: oil derivatives, soil, bioremediation, Isopoda

Representatives of Isopoda order inhabiting the soil environment are counted among decomposing soil macrofauna. They feed mainly on dead plant material. They contribute to accelerating the decomposition processes by mechanical and chemical crushing of plant tissues which they enrich in microorganisms during transport through their bowels [1, 2]. Due to their key role in the matter cycling, common occurrence and ease with which they are collected, they are frequently used in research on the environment risk assessment [3-5]. The investigations on the effect of water polluting oil derivatives point to their strong toxic effect on macroinvertebrate fauna, including crustaceans [6]. Considerably less information is available about this type of pollution effect on terrestrial crustaceans. As reported by Van Brummelen et al [7] mainly due to the food they consume, Isopods are exposed to toxic effect of PAHs, regarded as the most dangerous oil derivative substances. Strategies of avoiding the polluted soil by Isopoda are also well known, which argues for their possible use as bioindicators of pollution and assessment of bioremediation progress [4].

The research aimed at investigating the effect of oil derivatives during the process of their bioremediation on dynamics of Isopoda occurrence.

Materials and methods

The investigations were conducted in 2009-2012 at the Experimental Station of the University of Agriculture in Mydlniki near Krakow. In autumn 2009 indigenous soil was

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placed in 1 m^3 containers with maintained natural layers arrangement. The containers were then dug into the soil, so that their upper area was on the same level with the surrounding soil. The soil in containers was left untouched for 8 months to allow it to restore its natural biological efficiency. After this period (in June 2010) the soil in containers was polluted with the following oil derivatives: petrol, diesel oil and used engine oil in the amounts equal to 6000 mg of fuel · kg^{-1} d.m. of soil. A week later half of the containers was subjected to bioremediation with the use of ZB-01 biopreparation, specially prepared for this purpose. Four objects were identified in each of the two series (natural and supported bioremediation): 1. Control - unpolluted soil, 2. Soil with simulated petrol leak, 3. Soil with simulated diesel oil leak and 4. Soil with simulated used engine oil leak. The whole experiment was conducted in 4 replications according to randomized block design. Isopods were trapped using Barber's traps (0.9 dm^3 jars dug even with the soil level and protected against atmospheric precipitation with a plastic roof) placed in the central point of each container. During the periods from June to October 2010, from May to October 2011 and 2012 the traps were emptied once a week. Statistical computations concerning Isopoda occurrence in the subsequent months and years from the moment of soil pollution were made using Statistica 10.0 PL computer programme. Means were diversified using NIR Fisher test at significance level $\alpha = 0.05$.

Results and discussion

The dynamics of Isopoda trapping during the conducted research did not reveal the maximum of their occurrence during the vegetation season (Figs. 1-3). In 2010 the most numerous were trapped at the beginning of September, in 2011 by the end of May, at the turn of July and August and by the end of October, whereas in 2012 the course of the trappings fluctuated greatly. Isopoda activity is often connected with the substratum moisture. During the first three months following the soil contamination with oil derivatives, no significant effect on the number of trapped Isopoda representatives was registered (Table 1). In the fourth month significantly lower number of these crustaceans were noted in conditions of soil polluted with engine oil in comparison with the control, however next month more were caught in the polluted soil. Supported bioremediation applied on the soil polluted with diesel oil, as soon as in the fourth month after pollution revealed a marked effect contributing to increased number of trapped Isopoda.

In the second research period, *ie* 11-16 months after the contamination moment, a distinctive reduction of these invertebrate activity was observed under the influence of engine oil during their intensified occurrence (14th month following the contamination moment). Analysis of the oil derivative compounds content at that time pointed to their still about 5-fold higher content than the content of compounds extracted by light petroleum from the unpolluted soil (unpublished data). Supported bioremediation did not affect significantly Isopoda occurrence during this period. Analysis of results obtained for the entire vegetation period revealed a significant negative effect of engine oil, slightly reduced by the conducted supporting remediation. On the other hand, in case of soil polluted with petrol and subjected to supporting bioremediation, markedly smaller number of Isopoda were trapped than in the unpolluted soil (Fig. 4).

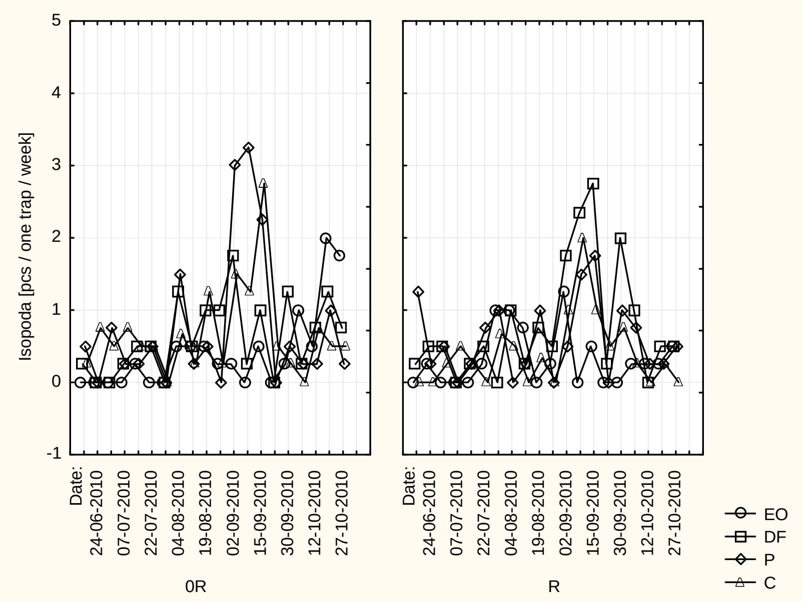

Fig. 1. Course of dynamics of Isopoda occurrence trapped using Barber's traps in 2010. EO - soil contaminated with used engine oil, DF - soil contaminated with diesel fuel, P - soil contaminated with petrol, C - unpolluted soil, 0R - series without bioremediation, R - series with bioremediation

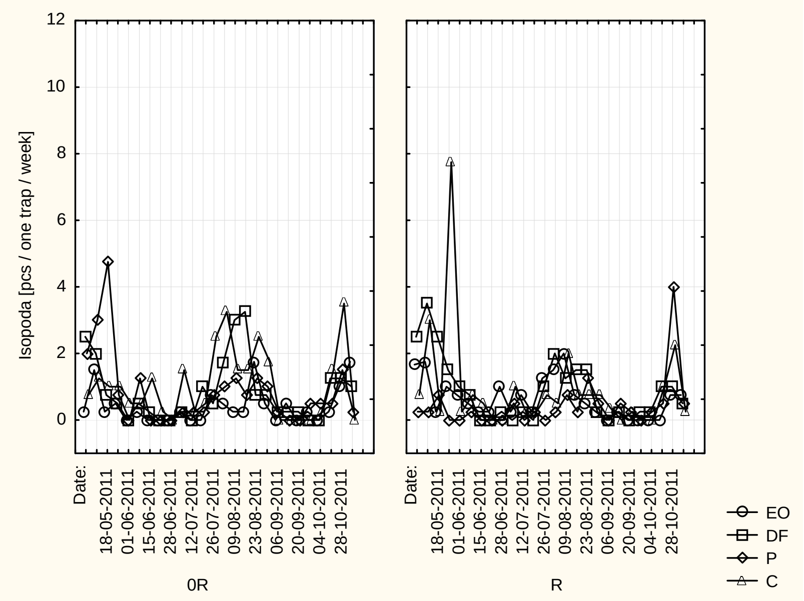

Fig. 2. Course of dynamics of Isopoda occurrence trapped using Barber's traps in 2011. The symbols as in Figure 1

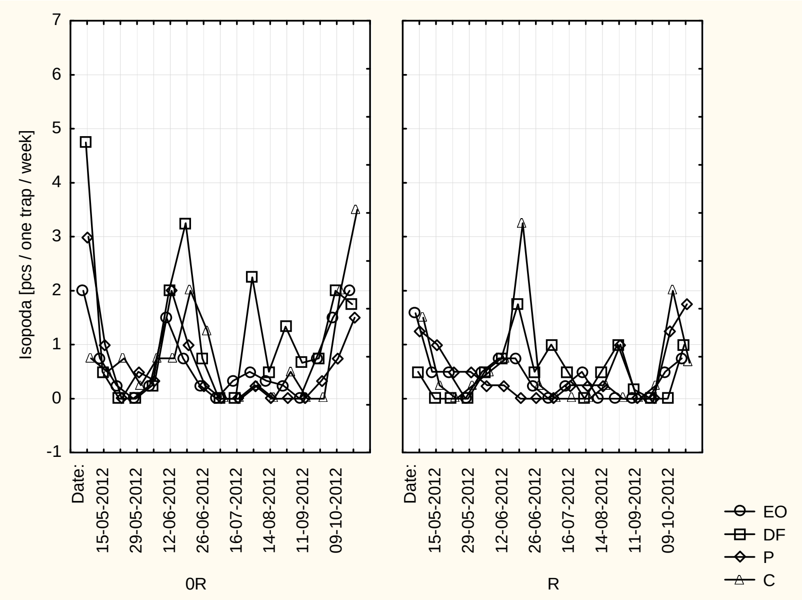

Fig. 3. Course of dynamics of Isopoda occurrence trapped using Barber's traps in 2012. The symbols as in Figure 1

Table 1

Occurrence of Isopoda trapped using Barber's traps in individual months after soil contamination. The symbols as in Figure 1

Number of months from the moment of soil contamination	**Isopoda [pcs/trap/month]**							
	Control		**Petrol**		**Diesel fuel**		**Engine oil**	
	0R	**R**	**0R**	**R**	**0R**	**R**	**0R**	**R**
1	2.25 a*	0.75 a	1.50 a	2.00 a	0.50 a	1.25 a	0.00 a	0.25 a
2	1.50 a	1.42 a	2.25 a	2.00 a	2.25 a	1.50 a	0.75 a	2.25 a
3	3.25 ab	1.33 a	3.75 ab	1.75 ab	4.25 b	3.25 ab	1.50 ab	2.25 ab
4	4.75 bc	4.25 ab	6.00 c	4.25 bc	2.50 ab	7.33 c	0.75 a	0.50 a
5	1.75 a	0.50 a	1.75 a	1.75 a	3.00 ab	2.00 a	5.25 b	1.25 a
11	4.50 a	12.00 a	10.50 a	1.25 a	5.75 a	11.00 a	2.50 a	5.42 a
12	2.00 a	1.25 a	1.25 a	0.25 a	0.75 a	1.00 a	0.25 a	2.00 a
13	4.75 a	2.25 a	1.50 a	0.75 a	1.75 a	1.25 a	1.00 a	2.50 a
14	10.50 b	4.75 ab	5.25 ab	3.00 a	9.50 ab	6.50 ab	3.25 a	5.00 ab
15	0.00 a	0.58 a	0.75 a	0.75 a	0.75 a	0.50 a	0.75 a	0.25 a
16	5.25 a	3.50 a	2.75 a	5.25 a	3.50 a	2.75 a	3.00 a	1.50 a
23	2.25 ab	2.00 ab	4.50 b	3.25 ab	5.25 b	0.50 a	3.00 ab	2.67 ab
24	4.75 b	4.75 b	3.58 ab	0.50 a	6.25 b	3.50 ab	2.75 ab	2.25 ab
25	0.25 a	0.00 a	0.25 a	0.50 ab	2.25 b	1.50 ab	0.83 ab	0.75 ab
26	0.50 ab	0.25 ab	0.00 a	1.25 ab	1.83 b	1.50 ab	0.58 ab	0.00 a
27	0.00 a	0.25 a	0.33 a	0.00 a	1.42 b	0.17 a	0.75 ab	0.00 a
28	5.50 b	2.67 ab	2.25 a	3.00 ab	3.75 ab	1.00 a	3.50 ab	1.25 a

* Means in lines marked with the same letters do not differ significantly according to NIR test at $\alpha = 0.05$; factors contamination x remediation

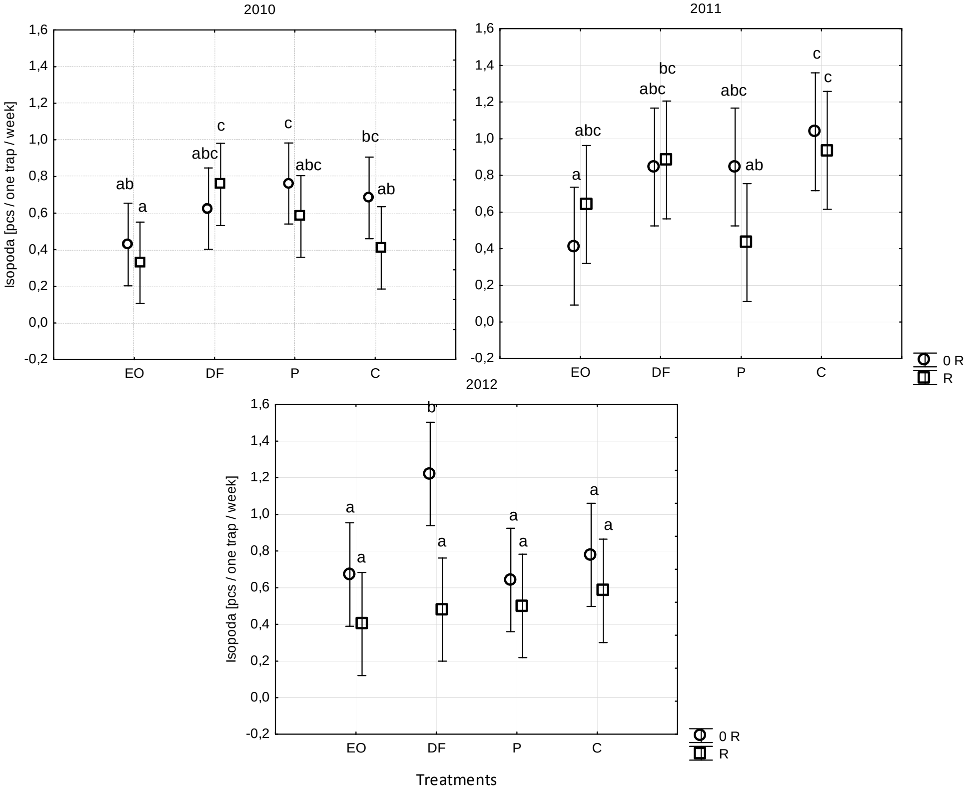

Fig. 4. Occurrence of Isopoda trapped using Barber's traps mean in the years 2010, 2011, 2012. The symbols as in Figure 1. Means marked with the same letters do not differ significantly according to NIR test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ±0.95 confidence interval

In the 2012 season (23-28 months after contamination) heightened Isopoda activity was observed in the soil contaminated with diesel oil (Figs. 3 and 4, Table 1). In this case bioremediation contributed to a decrease in the number of trapped Isopoda to the level similar to the control soil.

Research by Couceiro et al [8] demonstrated a very strong reduction of Isopoda representatives occurrence on the banks of a stream exposed to oil spill. In comparison with the banks of unimpacted stream, 19-fold less of this order representatives were found in the samples collected from the banks of polluted stream. Engine oil most negatively affected Isopoda occurrence, which is undoubtedly connected with the presence of hardly decomposable components, among others PAHs, whereas no significant effect of petrol on the analysed fauna was noted during almost whole period of investigations. This kind of pollutions becomes fast eliminated from the soil due to high content of volatile fractions. During the final period of research, *ie* after 2 years from the contamination, intensified activity of Isopoda was observed in conditions of soil contaminated with diesel oil. The reason might have been decreasing concentration of repellent substances proceeding in time and possibly the appearance of some attractant substances. As has been demonstrated by research of Zimmer et al [9] one of the most common Isopoda representatives - *Porcellio scaber* is able to identify food by olfaction. The species recognizes the smell of metabolites produced by the microorganisms colonizing leaves. One of the attractants is a by-product of cellulolytic activity of these microorganisms. Santos et al [4] stated an apparent avoiding of soil polluted with high doses of dimethoate, glyphosate and spirodiclafen by *Porcellionides pruinosus.* However, at lower doses of spirodiclofen, even attractant effect was registered. The authors explained it by a possible attractant effect of some substances included in the content of formulations.

Conclusions

1. Activity of Isopoda order representatives was reducing under the influence of soil pollution with engine oil - the result was discernible even after 14 months from the moment of contamination. Pollution with petrol generally did not affect the occurrence of Isopoda, whereas contamination with diesel oil even favoured their presence after two years from the contamination moment.
2. Supported bioremediation applied to the soil contaminated with diesel and engine oils was regulating, *ie* contributed to increase in the number of trapped specimens in places where the oil derivatives limited their occurrence (the object polluted with engine oil) or to diminish their activity where the soil pollution favoured the occurrence of crustaceans (the object where the soil was contaminated with diesel oil in the 2012 season). In result, the number of trapped Isopoda was similar as in the unpolluted object.

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ODDZIAŁYWANIE ZANIECZYSZCZENIA GLEBY ROPOPOCHODNYMI NA WYSTĘPOWANIE ISOPODA

Katedra Ochrony Środowiska Rolniczego, Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem pracy było zbadanie oddziaływania substancji ropopochodnych w trakcie procesu bioremediacji gleby na przebieg dynamiki występowania Isopoda. Utworzono następujące obiekty: kontrola - gleba niezanieczyszczona; gleba zanieczyszczona benzyną; gleba zanieczyszczona olejem napędowym oraz gleba zanieczyszczona zużytym olejem silnikowym (dawka: 6000 mg paliwa · kg^{-1} s.m. gleby). Eksperyment został przeprowadzony w dwóch seriach: z naturalną i wspomaganą bioremediacją. Bezkręgowce były odławiane z użyciem pułapek Barbera. W okresie od czerwca do października 2010 roku oraz od maja do października 2011 i 2012 roku pułapki były opróżniane raz w tygodniu. Aktywność przedstawicieli rzędu Isopoda ulegała ograniczeniu pod wpływem zanieczyszczenia gleby olejem silnikowym - efekt ten widoczny był jeszcze po upływie 14 miesięcy od momentu skażenia. Zanieczyszczenie benzyną nie wpływało na ogół na występowanie równonogich, zaś skażenie gleby olejem napędowym po upływie 2 lat od momentu zanieczyszczenia wręcz sprzyjało ich obecności. Bioremediacja wspomagana zastosowana na glebę skażoną olejami silnikowym i napędowym oddziaływała regulująco, tj. przyczyniała się do zwiększenia liczby odławianych osobników tam, gdzie ropopochodne ograniczały ich występowanie (obiekt zanieczyszczony olejem silnikowym), bądź do zmniejszenia ich aktywności tam, gdzie zanieczyszczenie gleby sprzyjało występowaniu skorupiaków (obiekt z glebą zanieczyszczoną olejem napędowym w sezonie 2012 roku). W rezultacie łowność Isopoda kształtowała się podobnie jak w obiekcie niezanieczyszczonym.

Słowa kluczowe: ropopochodne, gleba, bioremediacja, Isopoda

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Janina GOSPODAREK[1] and Milena RUSIN[1]

RESIDUAL EFFECT OF SOIL POLLUTION WITH OIL DERIVATIVES ON THE OCCURRENCE OF ACARINA

NASTĘPCZY WPŁYW ZANIECZYSZCZENIA GLEBY ROPOPOCHODNYMI NA WYSTĘPOWANIE ROZTOCZY

Abstract: The aim of the work was to determine the residual effect (*ie* after one year and two years) of soil contamination with various oil derivatives (petrol, diesel fuel and used engine oil) on the activity of terrestrial Acarina. Assessed was also the effect of assisted bioremediation process on the abovementioned invertebrates. Soil, placed in the containers (1 m^3), was polluted with 6000 mg of fuel kg^{-1} d.m. of soil in June 2010. A week later half of the containers was subjected to bioremediation with the use of ZB-01 biopreparation, specially prepared for this purpose. Epigeal fauna including Acarina was trapped using pitfall traps in the years 2011 and 2012. Two years after the moment of soil contamination with petrol, diesel fuel and engine oil on the level corresponding to the most frequently registered content in the soil medium polluted with oil derivatives, their negative effect on Acarina activity on the soil surface is still evident. Application of bioremediation supported with ZB-01 preparation significantly reduces the negative effect in case of the soil contaminated with petrol and to a lesser extend also in soil polluted with diesel fuel, whereas it contributes to a considerable intensification of Acarina activeness in the soil contaminated with used engine oil. The number of Acarina caught using pitfall traps may be strongly modified by the course of the weather conditions during respective vegetative seasons.

Keywords: oil derivatives, soil, bioremediation, Acarina

Due to their growing consumption, oil derivatives constitute increasingly more frequently identified environmental hazards [1]. Harmful effect of oil derivatives on the soil environment may persist for various periods of time, depending on the pollutant kind and dose. Both the conditions under which the contaminated soil self-purification occurs and possible applications of various methods of assisted bioremediation are important [2-5]. Although the effect of oil derivatives on soil invertebrates has been researched, particularly from the perspective of their use as bioindicators [6, 7], only scant information is available about the effect of assisted bioremediation process on these organisms [8]. As has been proved, bioremediation using specially selected microorganisms brings beneficial results in purification of soils contaminated with oil derivatives [9].

Soil Acarina play a significant role in metabolic processes [10]. They are also often indicated as bioindicators of environmental changes resulting from human activity [11, 12].

The paper aimed at determining the residual effect (*ie* after one year and two years) of soil contamination with various oil derivatives (petrol, diesel fuel and used engine oil) on the activity of terrestrial Acarina. Assessed was also the effect of assisted bioremediation process on the abovementioned invertebrates.

Materials and methods

The research was conducted in 2009-2012 at the Experimental Station of the University of Agriculture in Mydlniki near Krakow. In the experiment containers with

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a capacity of 1 m^3 were used. The containers were dug into the soil, so that their upper area was on the same level with the surrounding soil. In June 2010 the soil in containers was polluted with the following oil derivatives: petrol, diesel oil and used engine oil (dose 6000 mg of fuel · kg^{-1} d.m. of soil). A week later half of the containers was subjected to bioremediation with the use of ZB-01 biopreparation, specially prepared for this purpose. This treatment was repeated in the spring 2011. The experiment was performed in four replications. Four objects were created in two series (natural and supported bioremediation): 1. Control - unpolluted soil, 2. Soil contaminated with petrol, 3. Soil contaminated with diesel oil and 4. Soil contaminated with used engine oil. Epigeal fauna including Acarina was trapped using pitfall traps (0.9 dm^3 jars dug even with the soil level and protected against atmospheric precipitation with a plastic roof) placed in the central point of each container. The traps were emptied once a week during the periods from May to October 2011 and 2012. Statistical computations were made using Statistica 10.0 PL computer programme. Means were diversified using LSD test at significance level $\alpha = 0.05$.

Results and discussion

The dynamics of Acarina occurrence in 2011 and in 2012 was similar, but the number of individuals was higher in 2012 (Figs. 1, 2). The dynamics in 2011, *ie* one year after the soil contamination, pointed to their most intensive activeness in May and at the beginning of June (Fig. 1). In the later period they were caught only sporadically. Similar dynamics of their occurrence, with peak abundance in June was registered also in previous investigations [13].

Table 1

Occurrence of Acarina trapped using pitfall traps in individual months after soil contamination. The symbols as in Figure 1

Number of months from the moment of soil contamination	**Acarina [No. of individuals / trap / month]**							
	Control		**Petrol**		**Diesel fuel**		**Engine oil**	
	0R	**R**	**0R**	**R**	**0R**	**R**	**0R**	**R**
11	2.50 ab*	3.00 ab	0.50 a	1.75 ab	4.25 ab	2.50 ab	3.75 b	2.46 ab
12	0.00 a	0.25 a	0.50 a	0.50 a	0.25 a	0.50 a	0.50 a	0.00 a
13	0.00 a	0.00 a	0.25 a	0.25 a	0.00 a	0.00 a	0.00 a	0.00 a
14	0.25 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a
15	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.25 a	0.00 a	0.00 a
16	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a	0.00 a
23	87.25 ab	86.50 ab	6.25 a	73.50 ab	9.42 a	27.25 a	3.75 a	154. 25 b
24	57.50 ab	63.25 ab	13.17 a	84.25 ab	15.50 a	42.00 a	13.00 a	121.25 b
25	12.25 a	23.17 ab	13.25 a	26.25 ab	16.25 a	12.75 a	12.67 a	40.33 b
26	4.00 a	8.00 a	14.50 a	10.74 a	13.25 a	9.25 a	5.25 a	18.08 a
27	3.50 a	11.58 a	12.08 a	7.25 a	9.75 a	10.00 a	7.50 a	17.75 a
28	3.75 ab	4.17 ab	4.50 ab	8.00 b	1.00 a	1.75 a	3.75 ab	7.25 b

* Means in lines marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation

In the 11th month, from the moment of the soil contamination, the most numerous Acarina were caught in the soil contaminated with engine oil (Table 1), on the other hand significantly fewer of these animals were caught into the traps placed in the soil polluted with petrol. However, none of the registered values differed markedly from these noticed under conditions of control soil. The bioremediation process did not influence significantly the Acarina activeness on the soil surface either. The number of Acarina caught in the months from 12 to 16 was very low and no visible differences were noted between the investigated objects. Also, the data analysis for the 2011 season did not reveal any effect of the soil pollution with oil derivatives or bioremediation supported with ZB-01 preparation on the occurrence of Acarina on the soil surface (Fig. 3).

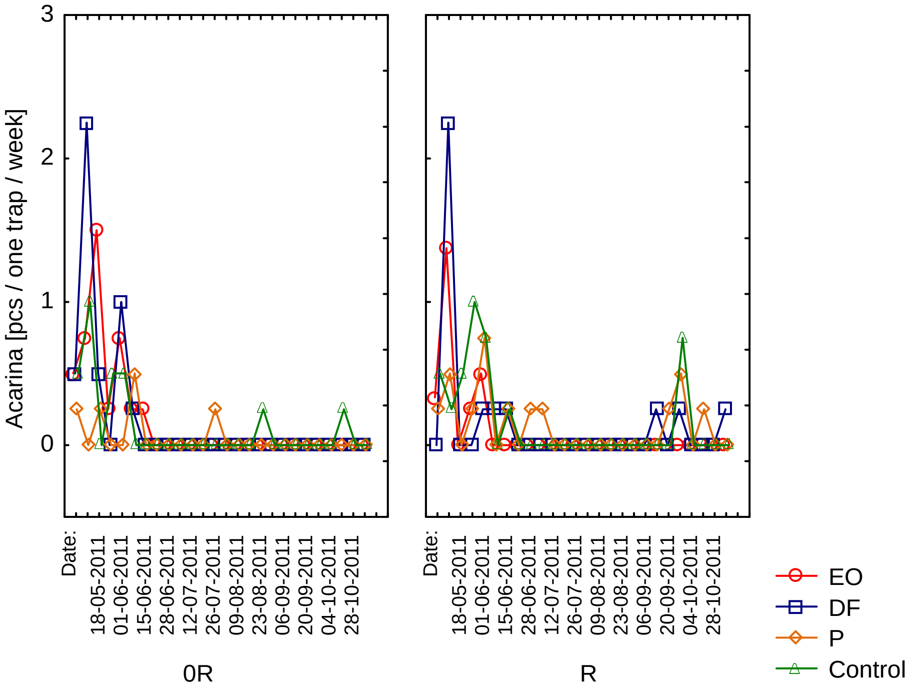

Fig. 1. Course of dynamics of Acarina occurrence trapped using pitfall traps in 2011. EO - soil contaminated with used engine oil, DF - soil contaminated with diesel fuel, P - soil contaminated with petrol, Control - unpolluted soil, 0R - series without assisted bioremediation, R - series with assisted bioremediation

Analysis of the dynamics of Acarina abundance in the 2012 season indicated their intensive activeness during the whole vegetation season (Fig. 2), with more intensive occurrence in May and June. According to Eyre et al [14], the meteorological conditions in a given season may have a considerable influence on the number of specimens caught using pitfall traps. In the months from 23rd to 25th from the moment of soil pollution, the highest numbers of Acarina were caught in the soil polluted with engine oil, but at simultaneously applied supported bioremediation (Table 1). Significantly fewer of these invertebrates were registered in all other objects with polluted soil, except the petrol contaminated soil subjected to bioremediation, whereas in the 25th month also in the control soil. In August and September 2012 (*ie* in the 26th and 27th month after contamination) Acarina number was much lower and no significant differences were noted at that time depending on the pollutant substance or the bioremediation. Heightened Acarina activity in the soil contaminated with petrol and engine oil after the application of biopreparation was registered also in October 2012 (the 28th month after the soil contamination).

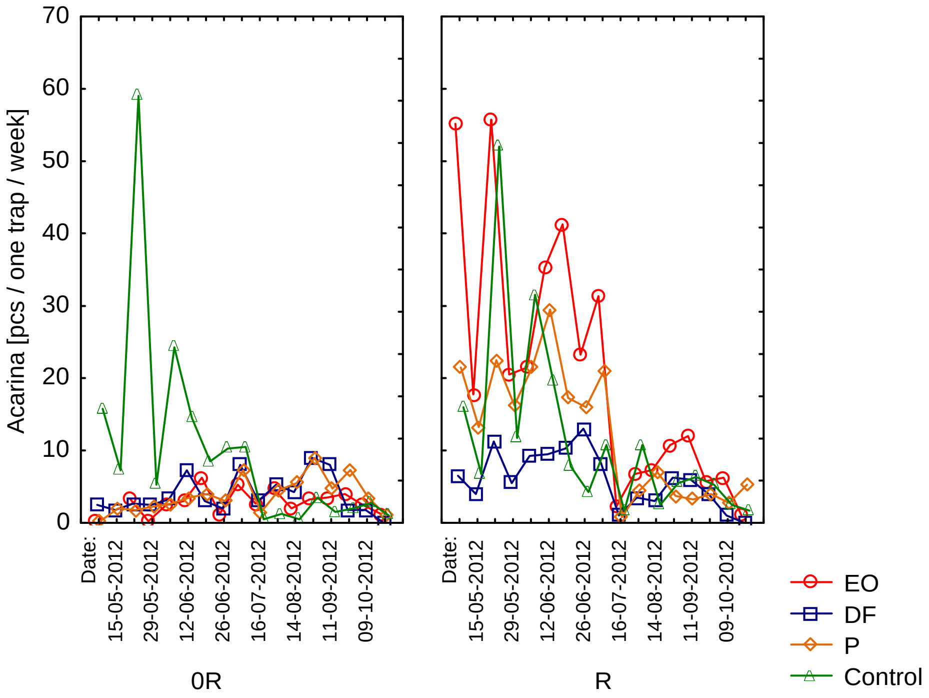

Fig. 2. Course of dynamics of Acarina occurrence trapped using pitfall traps in 2012. The symbols as in Figure 1

Joint analysis of the results obtained during the 2012 season revealed the persistent negative effect of the soil contamination with engine oil, diesel fuel and petrol regarding Acarina activeness on the soil surface. The applied supported bioremediation removed this negative effect in case of petrol as the pollutant substance. In case of diesel fuel, also increased number of caught Acarina was noted, so statistically it did not differ from the number registered in the control soil, where the biopreparation was not applied. In the soil contaminated with engine oil, the applied biopreparation led to a marked increase in the number of caught Acarina to the level almost twice higher than observed in the unpolluted soil without the biopreparation.

The research on the occurrence of terrestrial Acarina conducted in the presented experiment immediately after the soil pollution with oil derivatives (*ie* in the 2010 season) did not show any significant effect of the pollutants on the invertebrate activity on the soil surface [13]. On the other hand the applied biopreparation contributed to increased number of specimens caught in the soil contaminated with petrol 3 months after the contamination.

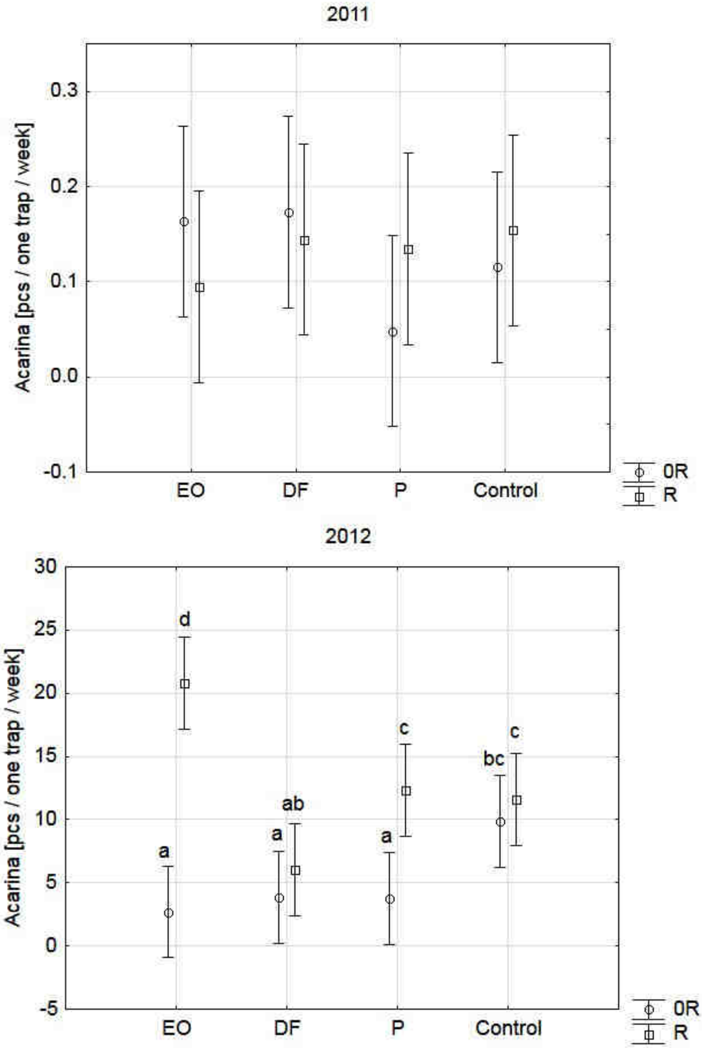

Fig. 3. Occurrence of Acarina trapped using pitfall traps mean in the years 2011, 2012. The symbols as in Figure 1. Means marked with the same letters do not differ significantly according to LSD test at $\alpha = 0.05$; factors contamination x remediation. ⌶ Mean ±0.95 confidence interval. In 2011 means do not differ statistically

In previous research, 2 and 3 years after the moment when crude oil was spilled on the roadside in result of a road disaster, slightly more numerous Acarina (Orbatida) were caught in the unpolluted area [15]. Investigations conducted by Blakely et al [16] as well as previous research of Ertsfeld and Snow-Ashbrook [17] also indicated a reduction in abundance of total Acarina with PAH contamination. The authors ascribe it to two possible reasons: fungicidal effect of PAHs, which reduces the amount of microarthropod's fungal or detrital food, or reduction of their habitat space due to increasing bulk density in effect of PAH contamination. On the other hand, Santarufo et al [18] mention the soil Acarina among the microarthropods fairly resistant to the urban environment.

Conclusions

1. Two years after the moment of soil contamination with petrol, diesel fuel and engine oil on the level corresponding to the most frequently registered content in the soil medium polluted with oil derivatives, their negative effect on Acarina activity on the soil surface is still evident.
2. Application of bioremediation supported with ZB-01 preparation significantly reduces the negative effect in case of the soil contaminated with petrol and to a lesser extend also in soil polluted with diesel fuel, whereas it contributes to a considerable intensification of Acarina activeness in the soil contaminated with used engine oil.
3. The number of Acarina caught using pitfall traps may be strongly modified by the course of the weather conditions during respective vegetative seasons.

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NASTĘPCZY WPŁYW ZANIECZYSZCZENIA GLEBY ROPOPOCHODNYMI NA WYSTĘPOWANIE ROZTOCZY

Katedra Ochrony Środowiska Rolniczego, Uniwersytet Rolniczy im. Hugona Kołłątaja w Krakowie

Abstrakt: Celem pracy było określenie następczego (tj. po upływie roku i 2 lat) oddziaływania skażenia gleby różnymi ropopochodnymi (benzyną, olejem napędowym i zużytym olejem silnikowym) na aktywność naziemnych Acarina. Ocenie poddano również wpływ procesu bioremediacji wspomaganej na wymienione bezkręgowce. Glebę umieszczono w kontenerach o pojemności 1 m^3 i zanieczyszczono 6000 mg substancji ropopochodnej kg^{-1} suchej masy gleby w czerwcu 2010 roku. Po upływie tygodnia połowa kontenerów z zanieczyszczoną glebą poddana została procesowi bioremediacji z użyciem preparatu ZB-01, specjalnie do tego celu przygotowanego. Faunę naziemną, w tym roztocza, chwytano z użyciem pułapek Barbera w latach 2011 i 2012. Po upływie 2 lat od momentu zanieczyszczenia gleby benzyną, olejem napędowym i olejem silnikowym na poziomie odpowiadającym najczęściej stwierdzanej zawartości w glebach średnio skażonych substancjami ropopochodnymi nadal widoczny jest negatywny ich wpływ na aktywność roztoczy glebowych na powierzchni gleby. Zastosowanie bioremediacji wspomaganej istotnie ogranicza ten negatywny wpływ w przypadku skażenia gleby benzyną i w mniejszym stopniu także olejem napędowym, a przyczynia się do znacznego zwiększenia aktywności roztoczy w warunkach gleby zanieczyszczonej zużytym olejem silnikowym. Liczebność roztoczy odławianych z użyciem pułapek Barbera może być silnie modyfikowana przebiegiem warunków pogodowych panujących w danym sezonie wegetacyjnym.

Słowa kluczowe: ropopochodne, gleba, bioremediacja, Acarina

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Katarzyna GRATA[1] and Małgorzata NABRDALIK[1]

ANTIFUNGAL EFFICACY OF *Bacillus amyloliquefaciens* AGAINST *Alternaria* sp.

SKUTECZNOŚĆ PRZECIWGRZYBOWA *Bacillus amyloliquefaciens* WOBEC *Alternaria* sp.

Abstract: The aim of the research was to assess a potential biological activity of *B. amyloliquefaciens* against *Alternaria* sp. In the conducted studies taken into account three factors: the bacterial cell density, the presence of the bacterial cells or the cell-free supernatant and the composition of the medium. The antagonistic properties were assayed with a dual culture plate method on PDA and Czapek media. The culturing process was conducted at 25 ±2°C for 14 days. The influence of the metabolites produced by *B. amyloliquefaciens* on the growth of *Alternaria* sp. was evaluate on the basis the growth rate index. Conducted studies have shown that the linear growth of *Alternaria* sp. was 6-fold and 5-fold slower after application of bacterial culture with the optical density equal 2.0, respectively on PDA and Czapek media, compared to the control tests. Furthermore, it was a slightly stronger inhibitory properties of *B. amyloliquefaciens* on PDA medium, wherein the carbon source was glucose than on Czapek medium where the carbon source was sucrose. This difference was about 1-3%. The linear growth of the fungus was inhibited more strongly by bacterial culture (approximately 2-3%), compared to the cell-free supernatant, regardless of the density of the cells and type of medium. Taking into account all the analyzed factors, the application of bacterial culture with a density of 2.0 on PDA medium, resulted in the slowest the growth of this fungus, approximately 83% compared with the control tests. *B. amyloliquefaciens* may find a wide range of application, in the process of plant protection against diseases caused by *Alternaria* sp.

Keywords: *Bacillus amyloliquefaciens, Alternaria* sp., fungistatic activity

Introduction

Fungi of the genus *Alternaria* are common in many parts of the world, they are cosmopolitan organisms and can be found in soil, plants, food and indoor air. Some of them are saprophytes, and others are pathogens of various crop plants, ornamentals, fruit and vegetables. They affected the various stages of the plant development resulting in, among others, seedling blight, leaf spot, root rot and diseases of various plants called alternariosis, contributing to significant economic losses. They also contribute to a significant reduction in seed yield and the spoilage of agricultural products during storage and during transport. [1-3]. Furthermore, *Alternaria* spp. produces dangerous to plants, animals and humans secondary metabolites with toxic properties (mycotoxins), among others, radicin (RAD), *epi*-radicinol (*epi*-ROH) by *A. radicina* and tenuazonic acid (TeA), altertoxin I, II, III (ATX I, II, III), alternariol (AOH) by *A. alternata* [1, 2, 4, 5]. One of most effective measures to control the disease caused by *Alternaria* sp. is effective application of fungicides [1].

More and more often in the plant crops strives to limit the use of pesticides because they are expensive, harmful to the environment and sometimes ineffective due to the immunization of pathogens. Intensive studies are being conducted on the possibility the introduction of new and safer methods to limiting the growth and development phytopathogens. Therefore, from year to year growing an interest in biological preparations

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using the non-pathogenic soil microorganisms of the genera *Bacillus* and *Psudomonas*. These microorganisms are known as PGPR (Plant Growth Promoting Rhizobacteria) that are able exert a beneficial direct or indirect effect on growth and development of plant. The direct impact of microorganisms is associated with enrichment of soil in nutrients and increasing their bioavailability for plants, synthesis the phytohormones or vitamins. Indirect effects result mainly from the improvement in the plant health by inhibiting the growth of pathogens and induction of resistance of plants to disease. The positive impact of the bacteria is possible due to the production by them the biological active metabolites *eg* antibiotics or cell wall degrading enzymes. Therefore, *Bacillus* spp. strains may be an alternative to the use of chemical substances, as according to the European Union Directives still seeks systematically to limit the use of chemicals in the environment [6, 7]. The aim of presented studies was to determine the biotic interaction of *Bacillus amyloliquefaciens* with the *Alternaria* sp.

Materials and methods

In this study the ability of the secondary metabolites produced by *Bacillus amyloliquefaciens* in limiting the growth of *Alternaria* sp. has been determined. The antagonistic properties of metabolites were assayed with a dual culture plate method on PDA medium consisting of [g/dm^3]: glucose 20.0, potato extract 4.0, agar 15.0 and on Czapek medium consisting of [g/dm^3]: sucrose 30.0, $MgSO_4 \cdot 7H_2O$ 0.5, KH_2PO_4 1.0, KCl 0.5, $NaNO_3$ 3.0, $Fe_2(SO_4)_3 \cdot 7H_2O$ 0,01, agar 15.0.

Fungal mycelial-disks (diameter of 10 mm) obtained from growing cultures of test fungal isolates were placed on the centre of this media inoculated with 0.5 cm^3 bacterial cells (BC) and cell-free supernatant (CFS) obtained from 24-hour culture of *B. amyloliquefaciens* at a different bacterial cell density (OD = 1.0 and OD = 2.0). In the control plates both of bacterial supernatants and bacterial culture were replaced with sterile broth medium. All plates were incubated at 25 ±2°C for 14 days. The colony diameters of the fungal pathogens in the test and the control plates were measured every 2-3 days until the mycelium of *Alternaria* sp. in the control plate, reached the edge of the plate. Each experiment was run in triplicate. The antagonistic activity of this bacterium was estimated as the growth rate index (T), calculated according to the formula below [8]:

$$T = \frac{A}{D} + \frac{b_1}{d_1} + \ldots + \frac{b_x}{d_x}$$

where A is the mean from colony measurement [mm], D is the experiment duration (number of days), $b_1 \ldots b_x$ is the increase a colony diameter from lasted measurement, $d_1 \ldots d_x$ is the number days from lasted measurement.

During the evaluation of the results was designated the percentage reduction of the growth rate index in the treated plate versus the growth rate index in the control plate.

Results and discussion

Several strains belonging to the genus *Bacillus eg B. amyloliquefaciens* and *B. subtilis* are able to excrete one or more compounds, among them bioactive non-volatile cyclic lipopeptides with fungistatic properties and the cell wall degrading enzymes. *Bacillus* *amyloliquefaciens* strains were reported effective for the biocontrol of multiple plant diseases caused by soilborne or post-harvest pathogens [9-11].

Therefore, the antifungal activity of *B. amyloliquefaciens* on 2 different media was evaluated toward tested *Alternaria* sp. Due to the fact that many of the factors determine the activity of the microorganisms in the conducted studies taken into account three: the bacterial cell density (OD), the presence of the cells or the cell-free supernatant and the composition of the medium. Conducted studies have shown differences in fungistatic activity of *B. amyloliquefaciens*, depending on the parameters analyzed.

It was observed that the linear growth of the mycelium of *Alternaria* sp. on the PDA medium was inhibited most efficient by adding both bacterial cells (BC) and cell-free supernatant (CFS) to the growth medium compared to the control test (Fig. 1). The value of the growth rate index for bacterial cells was similar when the optical density of the inoculum was 1.0 and 2.0 (7.31 and 7.54 respectively). The highest measured value (8.27) was recorded after application of the cell-free supernatant at optical density equal 1.0. The linear growth of *Alternaria* sp. was 6-fold slower on this medium compared to the control test.

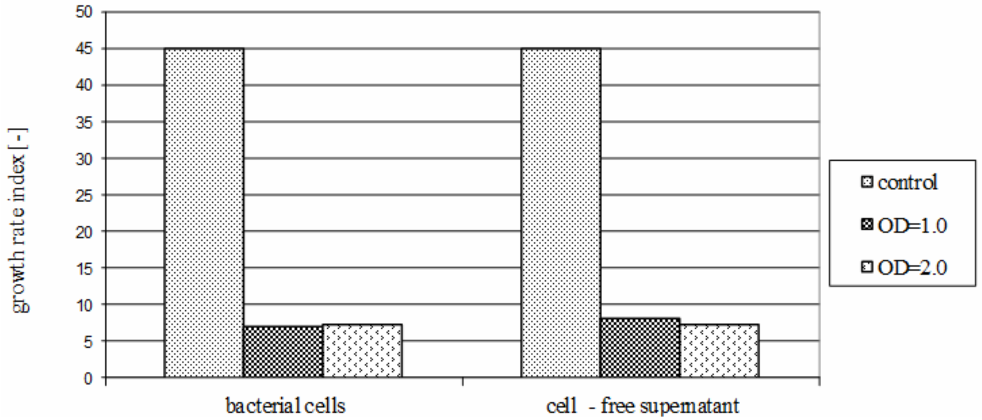

Fig. 1. Influence of *Bacillus amyloliquefaciens* on the growth rate index of *Alternaria* sp. on PDA medium (OD - optical density)

Similar activity of the metabolites of *B. amyloliquefaciens* against *Alternaria* sp. were observed on the Czapek medium with the sucrose. However, the inhibitory efficacy of this bacterium was slightly lower, when the cell-free supernatants were obtained from both inoculum with an initial optical density equal 1.0 and 2.0, compared to used the bacterial cells. The value of the growth rate index of *Alternaria* sp. amounted from 6.82 to 7.54 and was still 5-fold lower than the control test (41.07) (Fig. 2).

On both media, the difference in the inhibitory action of metabolites between the most and least acting culture of *B. amyloliquefaciens* amounted about 1.0-1.5 units.

The highest measured value of the growth inhibition was noted for the PDA medium, wherein as the carbon source was glucose than for the Czapek medium where as the carbon source was sucrose (Fig. 3).

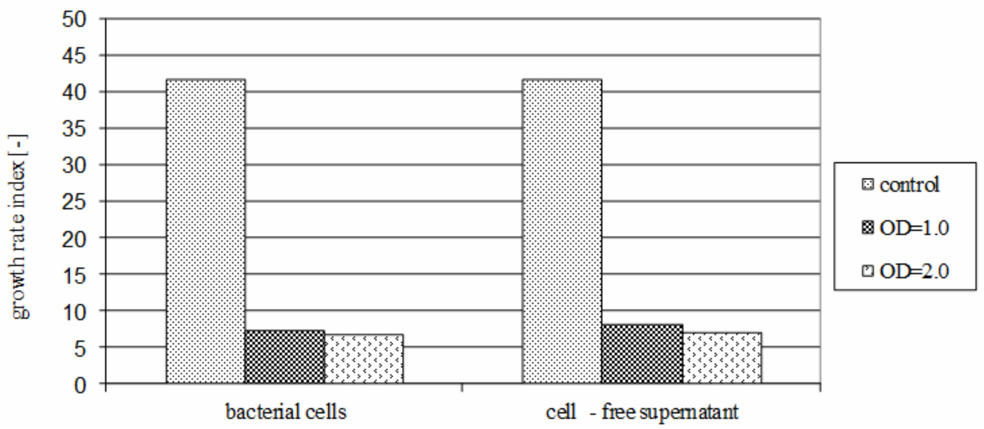

Fig. 2. Influence of *Bacillus amyloliquefaciens* on the growth rate index of *Alternaria* sp. on Czapek medium (OD - optical density)

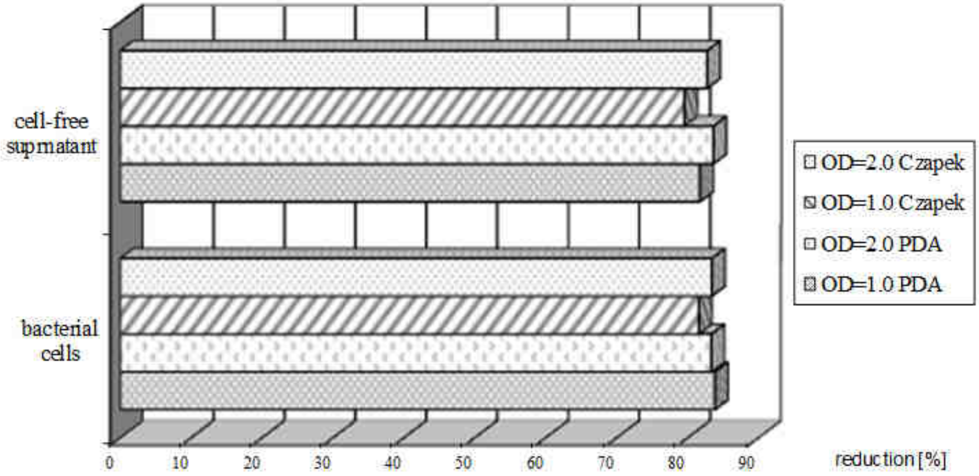

Fig. 3. Inhibition effect of *B. amyloliquefaciens* on mycelial growth of *Alternaria* sp.

The linear growth of the mycelium was inhibited most actively when the PDA medium was supplemented with the bacterial cells (optical density equal 1.0) and with the cell-free supernatant (optical density equal 2.0). The amounted obtained were: 83.85 and 83.60% respectively. Slightly lower activity of this bacterium was observed on the Czapek medium but it was still very high compared to the PDA medium. The inhibition of the growth of *Alternaria* sp. in case of both the bacterial cells and the cell-free supernatant for inoculum at initial optical density equal 2.0 ranged from 82.73 to 83.39 percent respectively. Taking into account all the analyzed factors, the application of bacterial culture with a density of 2.0 on PDA medium, resulted in the strongest inhibitory effect, by approximately 83%

compared with the control test. This might be due to production of metabolites secreted by this strain, diffused and dissolved into the culture media.

The possibility of controlling the soil-borne pathogens by introducing specific antagonistic bacteria to infected soil has been extensively investigated during the last decades. Extensive research has demonstrated that *Bacillus* spp. could have an important role in agriculture and horticulture in improving crop productivity. They have the capacity to colonize the rhizosphere and phyllosphere and to produce a broad spectrum of bioactive metabolites with antagonistic activity, among which are: cyclic lipopeptides (CLPs) of the surfactin, iturin and fengicin families [6, 7, 9, 12, 13]. Moreover, these bacteria are able to exhibit hyperparasitic activity, attacking pathogens by excretion lytic enzymes that can hydrolyze a wide variety of polymeric compounds, including chitin, protein, cellulose [7, 14]. Fungistatic activity is conditioned by many factors, primarily depends on the biological properties of the strain, susceptibility of the fungus and the number of the antagonist compared to the population of pathogen [15].

It is well known that production of most of antibiotics and its antagonistic properties are dependent on the composition of medium where the microorganisms is grown [16-18]. Fructose, sucrose and mannitol in the concentration 1% were better as carbon sources than glucose or glycerol for iturin A production [17]. Islam et al [18] reported that mannitol (1%) was selected as the optimum sources of carbon, for use in production of antibiotic substances by *B. subtilis* C9. The antifungal substance has been widely reported in *B. amyloliquefaciens* cultures [10]. For example, *B. amyloiquefaciens* FZB 42 is known to produce of both bacillomycin and fengycin which can suppress *F. oxysporium* [9]. Mitoi et al [19] observed drastic modification of cell structure, which can indicate a lytic effect of antagonistic bacteria against fungi, like degradation of membrane system, apparition of protuberance, formation of fibrous layer on the outer surface of the fungi cells, plasmalemmal detachment, constriction of cytoplasm and degradation of membrane system. The antifungal activity of iturin lipopeptides is related to their interaction with cytoplasmic membrane of terget cells leading to an increase in K^+ permeability [19, 20].

In addition, these substances not only inhibit the linear growth of colonies, but also inhibit the formation of spores or sclerotia. Inhibition of mycelial growth and production of morphological elements may significantly reduce the survival of pathogens in the soil [21]. *Bacillus amyloliquefaciens* strains were reported effective for the biocontrol of multiple plant diseases caused by soilborne or post-harvest pathogens. These bacteria can strongly inhibit the growth of many plant pathogenic fungi *eg Alternaria* sp., *Fusarium* spp., *Glomerella cingulata*, *Phytophthora drechsleri*, *Botritis cinerea* [15, 18, 19, 22]. According to Saideelfeen et al [23] the twenty seven of forty five *Bacillus* isolates displayed antagonism against *A. alternata* in-vitro, due to the production of antimicrobial compounds. Since the *Alternaria* species infect crops of economic importance, there is a strong need to effectively control for this pathogen.

Therefore *B. amyloliquefaciens* may be an alternative to the use of chemicals, as according to the directives of the European Union still seeks systematically to limit the use of chemicals in the environment.

Conclusions

The growth of *Alternaria* sp. was 6-fold and 5-fold slower after application of bacterial culture with a density of 2.0, respectively on PDA and Czapek media, compared to the control test. Furthermore, it was a slightly stronger inhibitory activity of *B. amyloliquefaciens* on PDA medium, wherein the carbon source was glucose than on Czapek medium where the carbon source was sucrose. This difference was about 1-2%. The linear growth of the fungus was inhibited more strongly by bacterial cells (BC) (approximately 1-3%), compared to the cell-free supernatants (CFS), regardless of the density of the cells and type of medium. Taking into account all the analyzed factors, the application of bacterial culture with a density of 2.0 on PDA medium, resulted in the slowest the growth of this fungus, approximately 83% compared with the control trial. Results obtained in this study suggested that *B. amyloliquefaciens* strain produced either a broad-spectrum antimicrobial compound or several bioactive compounds with different activities making it a potential candidate for use in the biocontrol of fungal plant diseases of agricultural importance.

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SKUTECZNOŚĆ PRZECIWGRZYBOWA *Bacillus amyloliquefaciens* WOBEC *Alternaria* sp.

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Abstrakt: Celem przeprowadzonych badań była ocena właściwości przeciwgrzybowych *B. amyloliquefaciens* wobec *Alternaria* sp. W badaniach uwzględniono trzy parametry: gęstość komórek bakteryjnych, rodzaj podłoża oraz wpływ hodowli zawierającej komórki bakterii lub płyn pohodowlany. Ocenę właściwości antagonistycznych metabolitów bakteryjnych przeprowadzono metodą hodowlano-płytkową z zastosowaniem podłoży Czapka i PDA. Hodowlę prowadzono w temp. 25 ±2°C przez 14 dni. Na podstawie indeksu tempa wzrostu określono aktywność fungistatyczną *B. amyloliquefaciens*. Badania wykazały różnice w aktywności metabolicznej bakterii w zależności od analizowanych parametrów. Liniowy wzrost *Alternaria* sp. był prawie 6-kronie słabszy na podłożu PDA i 5-krotnie słabszy na podłożu Czapka po zastosowaniu hodowli bakterii o gęstości E = 2,0. Ponadto nieznacznie silniejsze właściwości hamujące *B. amyloliquefaciens* odnotowano na pożywce PDA, w której źródłem węgla była glukoza, niż na pożywce Czapka zawierającej sacharozę. Różnica ta wynosiła około 1-3%. Liniowy wzrost grzyba był również silniej hamowany o ok. 2-3% po zastosowaniu hodowli bakteryjnej w porównaniu do supernatantu, niezależnie od gęstości komórek i rodzaju pożywki. Biorąc pod uwagę wszystkie analizowane czynniki, zastosowanie hodowli bakteryjnej o gęstości 2,0 i pożywki PDA spowodowało zmniejszenie tempa wzrostu tego grzyba o około 83% w porównaniu do próby kontrolnej. *B. amyloliquefaciens* może znaleźć szerokie zastosowanie w procesie ochrony roślin przed chorobami wywołanymi przez *Alternaria* sp.

Słowa kluczowe: *Bacillus amyloliquefaciens*, *Alternaria* sp., aktywność przeciwgrzybowa

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Joanna GUZIAŁOWSKA-TIC[1] and Wilhelm Jan TIC[1]

THE IMPACT OF AN IRON-BASED MODIFIER FOR LIQUID FUELS ON HUMAN HEALTH AND THE ENVIRONMENT

WPŁYW NA ŚRODOWISKO I ZDROWIE CZŁOWIEKA MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

Abstract: It is necessary to use specific modifiers in order to reduce harmful emissions arising in the combustion of liquid fuels into the atmosphere. Such modifiers include organic metal salts which are soluble in fuels and tend to form metal oxides under combustion process conditions, improving the oxidizing properties of fuels. The modifier, described in this paper was used in liquid fuel combustion tests, showing a desirable effect of reducing CO, NO_x and hydrocarbon emissions. For such modifiers to be approved for use, examination of their physico-chemical, toxicological and ecotoxicological properties is required according to REACH Regulation. REACH is intended, first of all, to provide appropriate protection to the environment and human health, while striving to maintain competitiveness of European enterprises in the global market. Discussed in this paper is the effect of an iron-based modifier for liquid fuels on human health and on the land and air and the aquatic environment. The modifier was subjected to physico-chemical analyses, and toxicological and ecotoxicological tests in accordance with good laboratory practice and OECD guidelines. The test results indicate that the modifier is a safe substance, posing no hazard to human health or the environment.

Keywords: fuel modifiers, toxicology, ecotoxicology, combustion, liquid fuels

Introduction

Fuel combustion processes generate harmful emissions into the atmosphere. Specific additives are used commercially in the power industry to reduce such emissions. Such additives include modifiers based on organic metal salts, dispersed in organic solvents, which are soluble without limitations in the combusted liquid fuels. Testing of the product is required, to determine its toxicological and ecotoxicological properties in connection with the intended launching of a facility producing 100 Mg per year of the modifier [1].

The toxicological tests are intended to assess any undesirable or harmful effect of chemical substances or other factors on living organisms, and to perform a probability analysis for their occurrence in various exposure conditions. Living organisms are exposed to the combined positive and negative effect of chemical substances and environmental conditions during their growth and development. The observed impact is the response of such living organisms to their exposure to all biologically active components [2, 3].

Ecotoxicological properties are established in examinations of organisms, populations, communities, biocenoses, and ecosystems in the aspect of their exposure to chemical factors, their penetration from the environment into the organisms, as well as any toxic effect that may occur. Ecotoxicology as a science deals with the impact of toxic substances on the biocenosis, especially on the parameters of the life cycle of organisms in natural conditions. Such life cycle parameters include: reproduction, lethality, life span, and maturing time [4].

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[*] Contribution was presented during ECOpole'14 Conference, Jarnoltowek, 15-17.10.2014

Discussed in this paper is the effect on human health and the environment of an iron-based modifier for liquid fuels. The necessary tests, enabling the assessment of risks to human health and the environment, were carried out, in accordance with Good Laboratory Practices, at the Institute of Industrial Organic Chemistry, Pszczyna, Poland.

Methodology

Assessment of environmental risks

Ecotoxicological tests were carried out on the example of respiration inhibition of micro-organisms in activated sludge according to OECD Guideline No. 209 (Method C.11) [5, 6]. The test was intended to assess the toxic effect of an iron-based modifier on micro-organisms in activated sludge. The test system was a mixture comprising water, a synthetic sewage feed, activated sludge, and a reference material solution.

Two sets of test samples were prepared in the initial experiment: one set comprising a nitrification inhibitor. A N-allylthiourea (ATU) solution at a concentration of 2.32 g/dm^3 was used for inhibiting nitrification.

Every test system included an abiotic control (sample F_A), experimental control (samples F_{B1}-F_{B2}), samples containing the test material (F_{T1}-F_{T5}) and samples containing the reference material (F_{R1}-F_{R5}). Activated sludge from a biological waste-water treatment plant was used as a microbial inoculum.

The respective amounts of the test material components are shown in Table 1.

Table 1

Amounts of components in the respective mixtures (test material: iron-based modifier)

Components of mixtures	**Amounts in test vessels**				
	F_{T1}	**F_{T2}**	**$F_{T3\text{-}5}$**	**$F_{B1\text{-}2}$**	**F_A**
Test material [mg]	5	50	500	0	500
Synthetic sewage feed [dm^3]	0.016	0.016	0.016	0.016	0.016
Activated sludge [dm^3]	0.25	0.25	0.25	0.25	0
Water [dm^3]	A volume of water was added to obtain a total of 0.5 dm^3 in every test vessel				
Total volume of mixture [dm^3]	0.5	0.5	0.5	0.5	0.5
Concentrations in the mixtures:					
of test material [mg/dm^3]	10	100	1000	0	1000
of activated sludge (suspended solids) [g/dm^3]	1.5	1.5	1.5	1.5	0

All mixtures were aerated intensely and incubated for three hours. The test material was used in the following concentrations: 10.0; 100.0; 1000.0 mg/dm^3. The reference material was used at the following concentrations: 0.5; 5.0; 10.0; 20.0; 50.0 mg/dm^3. Each sample was transferred into a BOD bottle after 3 hours and the concentration of oxygen was measured within 10 minutes using an oxygen electrode.

Oxygen consumption rate (*R*), as expressed in milligrams per liter per hour [mg/dm^3·hr], and specific respiration rate (R_S), as expressed by the amount of oxygen consumed by 1 gram of dry weight of the microbial activated sludge per hour [mg/g·hr], were calculated using the following formula:

$$R = (Q_1 - Q_2)/\Delta t \cdot 60 \qquad (1)$$

where Q_1 is the oxygen concentration at the beginning of measurement [mg/dm^3], Q_2 is the oxygen concentration at the end of measurement [mg/dm^3], Δt is the duration of measurement:

$$R_S = R / SS \tag{2}$$

where SS - suspended solids concentration, as found at the beginning of the experiment [g/dm^3].

Based on the data obtained from Equations (1) and (2), the inhibitory effect of the test material on micro-organisms in the activated sludge was measured. This enables the calculation of the value of EC$_{50}$, defined as the statistical effective concentration, which induces in the environmental sewage feed a respiration inhibition of 50% [2]. The value of EC$_{50}$ was calculated using the software ToxRat Professional 2.10

$$I = \left[1 - \frac{(R - R_A)}{R_B}\right] \times 100 \ [\%] \tag{3}$$

where I is the percentage of respiration inhibition, R is the oxygen consumption by the test sample [mg/dm^3·hr], R_A is the oxygen consumption by the abiotic control [mg/dm^3·hr], R_B is the oxygen consumption by the experimental control [mg/dm^3·hr].

Assessment of risks to human health

Toxicological tests were carried out according to OECD Guideline No. 405 (Method B.5) for the acute irritation/corrosion of the eye in rabbit [7, 8]. It was the objective of the test to provide information about the potential health risks, caused by the impact of the iron-based modifier on the eye.

Table 2

Grading of ocular lesions [6, 7]

Cornea (opacity: degree of density)	
No ulceration or opacity	0
Scattered or diffuse areas of opacity, details of iris clearly visible	1
Easily discernible translucent area, details of iris slightly obscured	2
Nacrous area; no details of iris visible, size of pupil barely discernible	3
Opaque cornea, iris is not discernible through the opacity	4
Iris	
Normal	0
Markedly deepened rugae, congestion, swelling, moderate hyperaemia or injection; iris is reactive to light	1
Hemorrhage, gross destruction, or no reaction to light	2
Conjunctiva - redness (refers to palpebral or bulbar conjunctiva; excluding cornea and iris)	
Normal	0
Some blood vessels hyperaemic	1
Diffuse, crimson color; individual vessels not easily discernible	2
Diffuse, beefy red	3
Conjunctiva - swelling (refers to eye lids and/or nictitating membranes)	
Normal	0
Some swelling above normal	1
Obvious swelling, with partial eversion of lids	2
Swelling, with lids about half closed	3
Swelling, with lids more than half closed	4

In the experiment, 0.1 cm^3 of the test material (iron-based modifier) was applied into the conjunctival sac of one eye of a test animal; the other eye, which remained untreated, served as a control. The test was carried out in three animals to confirm the actual irritant effect or absence of irritation.

For the duration of the experiment, the animals were subjected to daily general clinical observation in respect of disease incidence and lethality. Detailed clinical observations for any lesions in the cornea, iris and conjunctiva were assessed after the lapse of 1, 24, 48 and 72 hours from the application of the test material.

The scoring of acute irritation/corrosion of the eye was defined using the grading of ocular lesions (Table 2). The grading concerns lesions in the cornea, iris and conjunctiva.

Results

Assessment of environmental risks

After the experiment, the following calculations were made for every sample: oxygen consumption (R), specific respiration rate (R_S) and percentage of respiration inhibition (I) in micro-organisms from activated sludge by the test material (iron-based modifier). The test results are shown in Table 3.

Table 3

Results of tests for various concentrations of the iron-based modifier

	Oxygen consumption [$mg/dm^3 \cdot hr$]	**Specific respiration rate [$mg/g \cdot hr$]**	**Percentage of respiration inhibition in micro-organisms from activated sludge [%]**
Control	32.46	21.64	-
Test material concentration: 10 mg/dm^3	32.70	21.80	0.74
Test material concentration: 100 mg/dm^3	32.28	21.52	2.03
Test material concentration: 1000 mg/dm^3	31.94	21.29	3.08

It was established that the concentration of the iron-based modifier, causing 50% percentage of respiration inhibition in micro-organisms from the activated sludge (EC_{50}) was higher than 1000 mg/dm^3.

Assessment of risks to human health

Ocular lesions were observed in the conjunctiva in rabbits after application of the test material (iron-based modifier), although such changes were not detected in the iris or cornea. Clinical observation 1 hr after the test substance application detected diffuse crimson redness in the conjunctiva in three rabbits, accompanied by congestion of the nictitating membrane and circumcorneal injection. Moreover, minor conjunctival swelling and swelling of the nictitating membrane was found in rabbits 2 and 3, while swelling of the nictitating membrane alone was observed in rabbit 1.

24 hours after the test substance application, rabbits 1 and 3 showed hyperaemia of some blood vessels and of the nictitating membrane, while rabbit 2 showed diffuse crimson

redness, hyperaemia of the nictitating membrane and circumcorneal injection. In addition, swelling of the nictitating membrane was observed in rabbits 1 and 2.

Clinical observation 48 hours after the test substance application showed hyperaemia of some blood vessels and of the nictitating membrane in the conjunctiva in the three rabbits. 72 hours after the test substance application, no ocular lesions were found in the conjunctiva in rabbits 1 and 3 while only rabbit 2 continued to have hyperaemia of some of its blood vessels and of the nictitating membrane.

Table 4 shows grading of acute eye irritation/corrosion based on the grading scale referred to in Table 2, pursuant to OECD Guideline 405 (Method B.5). The effect of acute eye irritation/corrosion in rabbit was assessed based on average results observed after 24, 48 and 72 hours. Pursuant to the OECD Guideline, results observed 1 hour after the application of the iron-based modifier are omitted from such grading.

Table 4

Grading of acute eye irritation/corrosion

Rabbit	**Eye part**	**After**				**Average results after 24, 48 and 72 hours**
		1 hr	**24 hrs**	**48 hrs**	**72 hrs**	
1	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**1**	**1**	**0**	0.7
	Conjunctiva - swelling	1	**1**	**0**	**0**	0.3
2	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**2**	**1**	**1**	1,3
	Conjunctiva - swelling	1	**1**	**0**	**0**	0.3
3	Cornea	0	**0**	**0**	**0**	0.0
	Iris	0	**0**	**0**	**0**	0.0
	Conjunctiva - redness	2	**1**	**1**	**0**	0.7
	Conjunctiva - swelling	1	**0**	**0**	**0**	0.0

Analysis of the test results

Assessment of environmental risks

The results of tests of the iron-based modifier indicate that, in experimental conditions in a test concentration range from 100 to 1000 mg/dm^3, the test material shows an inhibitory effect on respiration of micro-organisms in activated sludge. The test material concentration for which 50% respiration inhibition of micro-organisms in the activated sludge was observed (EC_{50}) is higher than 1000 mg/dm^3.

Respiration rate in the control was R_S = 21.64 mg/g·hr (Table 3), which seems a reliable result because it is higher than the limiting result of 20 mg of oxygen per gram of activated sludge per hour.

Assessment of risk to human health

After application of the test material (iron-based modifier), no ocular lesions were detected in the cornea and iris while the conjunctiva of the test animals showed only temporary lesions. Average results after 24, 48 and 72 for the conjunctiva (in three rabbits) were 0.9 for the redness and 0.2 for the swelling.

Based on the above results, it was found, pursuant to Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures, that the iron-based modifier for liquid fuels has no irritant effect on the eye in rabbit [9].

Moreover, pursuant to Regulation of the European Parliament and of the Council (WE) No. 1272/2008 of 16 December 2008 on the Classification, Labelling and Packaging of Substances and Mixtures (CLP), the iron-based modifier for liquid fuels is not categorized which means, it is not a hazardous substance and poses no risk to human health [10].

Summary and conclusions

This paper presents the results of toxicological and ecotoxicological tests on two selected examples. The toxicological results are discussed using the example of acute eye irritation/corrosion test in rabbit. No ocular lesions were observed in the cornea or in the iris while only temporary lesions were detected in the conjunctiva.

Ecotoxicological tests are discussed on the basis of the percentage of respiration inhibition in activated sludge. The test results indicate that the modifier's concentration causing 50% respiration inhibition in micro-organisms in activated sludge is higher than 1000 mg/dm^3.

Other results of toxicological and ecotoxicological tests indicate that the test iron-based modifier for liquid fuels is a safe substance, posing no risk to human health or the environment. Such tests, although not discussed in this paper, are going to be used for preparing registration documents for the product under REACH.

Based on the test results and pursuant to the Annex to the Regulation of the Minister of Health of 10 August 2012 on the criteria and methods for the classification of chemical substances and mixtures [9], the iron-based modifier for liquid fuels is found to be a safe substance, posing no risk to human health and to the land and air and the aquatic environment.

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WPŁYW NA ŚRODOWISKO I ZDROWIE CZŁOWIEKA MODYFIKATORA ŻELAZOWEGO SPALANIA PALIW CIEKŁYCH

Wydział Mechaniczny, Politechnika Opolska

Abstrakt: W celu ograniczenia emisji szkodliwych produktów spalania paliw ciekłych do atmosfery występuje konieczność stosowania specyficznych modyfikatorów. Jednym z nich są rozpuszczalne w paliwie organiczne sole metali, które w warunkach procesu spalania tworzą tlenki metali poprawiające własności utleniające paliw. Opisany modyfikator zastosowany został w testach spalania paliwa ciekłego, gdzie wykazał korzystny wpływ w ograniczeniu emisji węglowodorów, CO i NO_x. Dopuszczenie do stosowania wyżej wymienionych modyfikatorów wymaga określenia ich własności fizykochemicznych, toksykologicznych i ekotoksykologicznych w ramach rozporządzenia REACH. Najważniejszym celem tego rozporządzenia jest zapewnienie właściwej ochrony zdrowia ludzkiego i środowiska przy jednoczesnym dążeniu do zachowania konkurencyjności europejskich przedsiębiorstw na światowym rynku. W pracy przedstawiono wpływ na zdrowie człowieka oraz na środowisko wodne, lądowe i powietrzne modyfikatora żelazowego do paliw ciekłych. Badania fizykochemiczne, toksykologiczne i ekotoksykologiczne tego dodatku wykonane zostały zgodnie z dobrą praktyką laboratoryjną oraz wytycznymi OECD. Na podstawie uzyskanych wyników badań stwierdzono, iż badany modyfikator jest substancją bezpieczną i niestanowiącą zagrożenia dla zdrowia człowieka oraz środowiska.

Słowa kluczowe: modyfikatory paliw, toksykologia, ekotoksykologia, spalanie, paliwa ciekłe

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CHARACTERISTICS OF PELLETS MADE FROM DIFFERENT PLANT MATERIALS

CHARAKTERYSTYKA PELETÓW WYKONANYCH Z RÓŻNYCH MATERIAŁÓW ROŚLINNYCH

Abstract: The aim of this research was estimation of the characteristic properties (energy and qualitative) of pellets, which were made from different plant biomass. In this research the spruce wood sawdust pellets, straw wheat pellets, straw rape pellets and hay pellets (produced in a large scale companies) were used. In addition, in this research the same kinds of these pellets were used, but produced in domestic conditions. The analyses were conducted in the laboratory of the Faculty of Mechanical Engineering University of Žilina, in February 2014. The following parameters were analyzed: moisture content, total heating value (calorimeter LECO AC 500 was used) and calorific value. The aim of the qualitative evaluation of these pellets, water test was conducted and mechanical durability was estimated. The research indicated that the spruce wood sawdust pellets and straw rape pellets (produced in a large scale companies) were characterized the lowest moisture content (respectively 6.88 and 6.91%) (this is main parameter, which influences on energetic value of pellets) and the highest values of total heat (respectively 20.16 and 18.65 MJ/kg). The highest content of moisture and the lowest energetic value characterized the every pellets, which were produced in domestic mill.

Keywords: pellets, total heating value, biomass

Introduction

The development of renewable energy constitutes a crucial role for the future. Many studies in this field are conducted on the whole world. One of the main sources of this energy is plant biomass. The conducted studies indicate that biomass plant will be basic sources of renewable energy in the coming years [1]. The easy process of the biomass combustion and easy availability of this material cause that plant biomass becomes a competitive for fossil fuels [1-3]. In addition, combustion of the plant biomass causes reduction of sulfur oxides and nitrogen oxides [4, 5]. Pellets are usually produced from a variety of residue feedstocks, for example: straw, sawdust, wood (agricultural and forest biomass). They are produced from shell of some fruits and seeds, too. They are easy to store and transport [6-8]. It can cause that they are relatively cheap and they may also be used for production of energy through combustion, gasification and other chemical conversion processes [9, 10]. They are cylinders with a diameter of 6-10 mm and a length of 10-50 mm manufactured from raw wood (chips, sawdust). They are made by compression process called pelletizing [11, 12]. They don't usually contain chemical additives [11, 13]. Sometimes, pellets contain additives, for example limestone [14], dolomite, diatomite and potato starch [15, 16]. These additives are used for improve their qualitative and calorific properties. In opinion Ewida et al [17] addition kaolin to pellets can

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improve their sintering characteristics. The production of pellets in Slovakia achieved 120 000 Mg in 2008 year in turn, in Poland production of pellets in 2008 achieved 400 000 Mg, which 220 000 Mg were exported [8]. It indicates the development this sectors of the economy.

The aim of this research was evaluation of the characteristic properties (energy and qualitative) of pellets, which were made from different plant biomass.

Methods

In this research were used different types of biomass pellets:

- the spruce wood sawdust pellets (SWSP)
- the straw wheat pellets (SWP)
- the straw rape pellets (SRP)
- the hay pellets (HP).

These pellets were produced in large scale companies. These companies have usually perfect working automatic technology and it can work with no failures. Pellets made by them have appropriate certifications [18]. Cost of these pellets is usually very high.

Sometimes some people, who want to save money, produce pellets in domestic conditions. These pellets have usually the lower quality, because used pressures of compression are much lower. For comparison, in this research pellets produced on experimental domestic pellet mill were presented. There were:

- the spruce wood sawdust pellets ex (SWSP ex)
- the straw wheat pellets ex (SWP ex)
- the straw rape pellets ex (SRP ex)
- the hay pellets ex (HP ex).

The aim of the energetic estimation of these pellets the following parameters were determined:

- Moisture content - it was measured according to EN 14774; it was used drying analytical scale RADWAG 50 SX. A sample of pellets (approx 10 grams) was placed on a metal plate in the analytical scale. Then it has been recorded the wet pellets weight. The sample was dried at about 120°C [11] and after that it was recorded the dry pellets weight. The moisture content of the tested samples was estimated based on the weight difference (between the wet pellets weight and the dry pellets weight). The 2 measurements were made for each sample. The result of the moisture content was the average value.
- Total heating value - it was determined according to ISO 1716 by using of calorimeter LECO AC 500. The tested samples of pellets with weight about 1.0 g were burned in combustion vessel, which was filled with oxygen to a pressure 31.0 bar. Combustion vessel was immersed in 2.0 dm^3 of distilled water. During burning of the samples, the increasing temperature of water was measured.

  Calorific value of fuel, Q_i - it was calculated based on the following formula [11]:

$$Q_i = 18.84 - 0.217 \cdot w \tag{1}$$

where w - moisture content of fuel.

The aim of the qualitative evaluation of these pellets the following parameters were determined:

- Water test - this method allows only approximate qualitative assessment of pellets and serves only to compare different pellets (which are made from various plant biomass). This method based on the measurement of the total disintegration time of chosen pellets. From each sample two large pellets at the same size were selected. These pellets were placed in a glass beaker filled with water of about 0.2 dm^3. Then the disintegration time was measured until the pellets have disintegrated completely. The longer the disintegration time of pellets was indicated higher quality of these pellets.
- Mechanical durability (DU test) - this parameter is a measure of biofuel resistance on the impacts and abrasion, which are caused by transport and transhipments [6, 19]. This parameter was determined according to EN 15210 by using of special device - LignoTester (Fig. 1). There 100 g of pellets sample placed in stream of air for 60 s with pressure of air 70 mbar and after this was sample weighted.
- Amount of fines (F test) - this parameter was also measured in Lignotester (Fig. 1), where samples were placed in stream of air for 30 s with pressure of air 30 mbar. After this was weighted amount of fines under the sieve. Fines should preferably be less than 1% by weight. If fines arrive in the burning chamber, the flame may get too hot as fines particles burn faster than pellets. In the worst case the ash might sinter, which means that the burner must be cleaned after it has cooled down.

The high quantities of fines are produced in the storage system. It can cause operational failures. In turn, minimal amounts of fines in the storage system indicate on a high quality of pellets [3, 20].

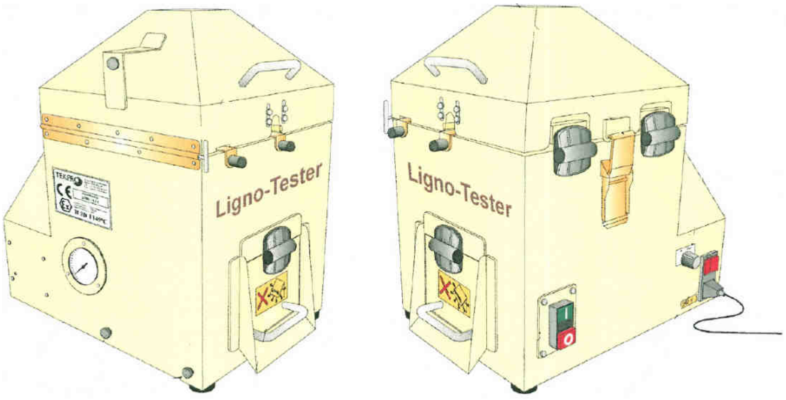

Fig. 1. Lignotester [21]

Results

As a result of conducted research was ascertained, that the spruce wood sawdust pellets and straw rape pellets were characterized the lowest moisture content (respectively 6.88 and 6.91%). This value of moisture content is very good, because commercially made pellets have normally moisture content about 7-10%. These pellets were also characterized the highest values of total heat (respectively 20.16 and 18.65 MJ/kg) and the highest values of calorific values (respectively 17.35 and 17.34 MJ/kg) (Fig. 2). These values depend on input material properties, kind of pellets and preparation technique, too (not only moisture content) [6].

For comparison, there was presented the results of the pellets, which were made at the domestic conditions. These results are very interesting. The SWSP ex achieved the high value of moisture content (9%), but the values of total heat were almost the same how straw rape pellets (18.67 MJ/kg).

Other pellets made at the experimental conditions were characterized by highest values of moisture content (9.6% for SRP ex, 10.2% for SWP ex and 10.3% for HP ex) and at the same time they achieved the very low values of total heat (respectively 18.11, 18.01 and 17.94 MJ/kg) and calorific values.

It can indicate that SWSP ex pellets were made from better input material during production than others.

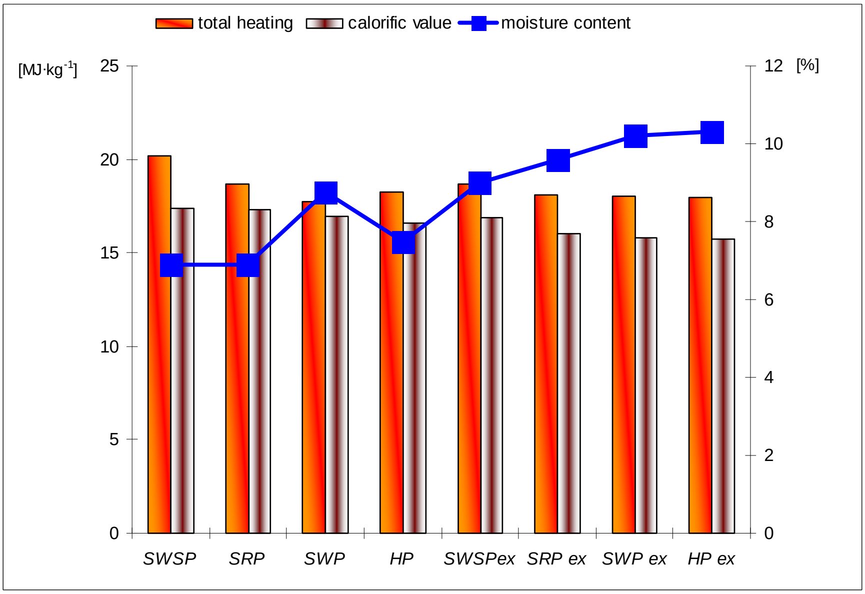

Fig. 2. Moisture content [%], total heating value [MJ·kg^{-1}] and calorific value [MJ·kg^{-1}] of pellets samples

The results of qualitative analysis indicated that the straw wheat pellets and straw rape pellets were characterized the longest time of disintegration in water test (respectively 20 and 18 min). Very interesting results were received for the SWSP and SWSP ex (there was decay after respectively 4 and 1.5 min) and for the HP and HP ex (there was decay after respectively 6 and 1 min) (Table 1). It can indicate that these kinds of pellets were characterized by the bad quality.

In contrast to the relatively high energetic values, these pellets achieved very poor quality in water test. Pellets with good quality can achieve 15-20 minutes disintegration time. These pellets disintegrated after very short time. It is probably caused by bad conditions of packaging and lack of or poor of assemblage binder (for example glycerol, lignin and dolomite). The suitable content of binder improves their molecular structure and influences on final quality of product.

DU test showed that every pellets produced in a large companies achieved the high mechanical strength, which was oscillated between: 97.6% in DU test (SWSP and HP) and 99% in DU test (SRP). In turn, pellets produced in domestic conditions achieved the lower values. They were oscillated between: 91.1% in DU test (SWSP ex) and 57.6% in DU test (HP ex) (Table 1).

The lower values of abrasion durability for these pellets can result from bad conditions of storage and transport. If there was the high of temperature in storehouse, it could influence on the lower mechanical strength.

Part by weight of the small particles (F test) oscillated between 0.05% (SRP) and 0.34% (SWSP). It was ascertained that pellets, which were made in experimental conditions, were characterized by the higher percent participation the small particles (0.92% in F test for SWSP ex and 7.27% in F test for HP ex) (Table 1). The high last values can result from bad quality of packaging. If the pellets are packed loosely, probably they will move and wipe out for each other. Then can arise the greater fraction of fine dust. The worst results were obtained for both types of hay pellets (both in DU test and F test).

Differences between pellets produced in large companies and domestic conditions are caused by pressure difference in production. Pellets produced of experimental domestic pellet mill don't achieve high pressure of compression. It probably causes crushing and shredding of pellets.

Table 1

Quality parameters of pellets samples

Samples	**DU test**	**F test**	**Water test (disintegration time)**
Unit	**[%]**	**[%]**	**[min]**
SWSP	97.6	0.34	4
SWP	98.9	0.12	20
SRP	99	0.05	18
HP	97.69	0.274	6.30
SWSP ex	91.1	0.92	1.5
SWP ex	69.02	3.75	3
SRP ex	78.69	2.81	3.40
HP ex	57.69	7.274	1.10

Discussion and conclusions

The conducted research expressly indicated that the best quality properties (DU test and F test) achieved straw rape pellets produced in large companies. In turn, the spruce wood sawdust pellets ex achieved the best quality properties from pellets made of domestic mill. Other pellets from this group characterized the significantly worse quality (DU test and F test mainly indicated for this).

The best calorific properties achieved three groups of pellets: SRP and both SWSP and SWSP ex. The similar results referring to straw rape pellets were achieved by Kachel-Jakubowska et al [19]. The best quality and calorific properties of straw rape pellets investigated by her were achieved. In opinion Jakubiak and Kordylewski [22] the significance of straw rape pellets increases and will grow, because they are useful for combustion in the different kinds of boilers (for example dust boilers and grate boilers). The good quality of different pellets depends on the content of moisture and the method of stored [3].

In turn, the worst calorific properties characterized the every pellets, which were made of domestic mill. These pellets stand out the relatively high water content (9% - SWSP ex, 10.3% - HP ex). This feature influenced on deterioration of the energetic properties of these pellets. The every pellets produced in domestic conditions were characterized by very short disintegration time in water test. This time oscillated between 1.10 min (HP ex) and 1.5 min (SWSP ex). It was probably result the lack of good binder or small its contents. In opinion Holubcik and Jandacka [21], Sarenbo and Claesson [14] the addition of talc, dolomite and limestone to wood pellets causes improve qualitative structure and extension of pellets disintegration time.

Pellets without good binder easily can be liable crushing and shredding during packaging and transport [14, 23]. The every pellets produced in domestic conditions achieved the worst abrasion resistance (91.1% - SWSP ex and 57.6 - HP ex in DU test) and the highest amount of small particles (respectively 0.92% and 7.27% in F test). The relatively high amount of small particles can influence on that the part of the fuel can fly to flue gas. It can result from bad packaging methods [24]. In conclusion, it can be said, that pellets, which are produced in experimental domestic pellet mill didn't achieve good quality.

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CHARAKTERYSTYKA PELETÓW WYKONANYCH Z RÓŻNYCH MATERIAŁÓW ROŚLINNYCH

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Abstrakt: Celem badań była ocena charakterystycznych (energetycznych i jakościowych) właściwości peletów, wykonanych z różnorodnej biomasy roślinnej. W badaniach wykorzystano: pelety wykonane z trocin drzewnych świerkowych, słomy pszenicznej, słomy rzepakowej oraz z siana (produkowane w dużych firmach). Dodatkowo w badaniach tych wykorzystano te same rodzaje peletów, ale produkowanych w warunkach eksperymentalnych. Analizy prowadzono w laboratorium Katedry Techniki Energetycznej Uniwersytetu Żylińskiego w Żylinie w lutym 2014 r. Brano pod uwagę następujące parametry: zawartość wilgotności, ciepło spalania (wykorzystano kalorymetr LECO AC 500) oraz wartość opałową. W celu oceny jakościowej badanych peletów przeprowadzono także test wodny oraz zbadano ich mechaniczną wytrzymałość. Badania wykazały, że najniższą wilgotnością (główny parametr wpływający na wartość energetyczną peletów) charakteryzowały się pelety wykonane z trocin drzewnych świerkowych oraz słomy rzepakowej (odpowiednio 6,88 i 6,91%) (ale produkowanych na dużą skalę w wielkich firmach) i uzyskały też najwyższą wartość ciepła spalania (odpowiednio 20,16 i 18,65 MJ/kg). Najwyższą zawartością wilgotności i najniższymi energetycznymi właściwościami cechowały się wszystkie pelety, które były produkowane w warunkach eksperymentalnych.

Słowa kluczowe: pelety, ciepło spalania, biomasa

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CONVERSION OF DIETHYLAMINE INTO NITROGEN OXIDES DURING COMBUSTION IN CHEMICALLY ACTIVE FLUIDIZED BED

KONWERSJA DIETYLOAMINY DO TLENKÓW AZOTU PODCZAS SPALANIA W AKTYWNYM CHEMICZNIE ZŁOŻU FLUIDALNYM

Abstract: Combustion processes of gaseous fuel (propane) without and with addition of various amounts of diethylamine in fluidized bed, made of chemically active calcium oxide, were run and studied. On the basis of registered temperature, dynamic pressure in reaction zone and composition of exhaust fumes, analysis of diethylamine conversion into nitrogen oxides and its influence on kinetics of propane combustion process was carried out. The complexity of solid fuels (alternative or biomass which can contain large amount of nitrogen compounds in a form of amines, heterocyclic compounds, amino acids etc.) combustion caused that at this phase of researches, incineration of gaseous fuel was run. Amine was dosed into the reaction zone in such amounts, which could give similar nitrogen oxides concentration in exhaust fumes, to those registered from combustion of alternative fuels with high nitrogen content (circa: 900, 1800, 3250 ppm). Results of experimental works revealed that up to 78% of nitrogen compound was converted to N_xO_y. The conversion rate was higher when greater amounts of $(C_2H_5)_2NH$ were dosed into reaction zone. The main nitrogen oxide created within combustion was nitric oxide, which constituted more than 95% of total N_xO_y. The remaining amount of amine was converted into nitrogen. $(C_2H_5)_2NH$ influenced on kinetics of the propane combustion process in noticeable way, but this impact was also limited. Diethylamine and products of its conversion, such as radicals present in the combustion zone, influenced on oxidization reactions of carbon monoxide and volatile organic compounds.

Keywords: nitrogen oxides emission, fluidised bed combustion, alternative fuels combustion, biomass combustion

Increasing energy demand causes, that fuels alternative to conventional *ie* biomass or wastes, are more often applied as a sources of energy in combustion processes next to fossil fuels (coal, gas, oil) which are still main energy sources. Combustion processes must be carried out in the most effective way from economical and what is very important environmental point of view. Combustion of materials such as biomass and wastes entails various types of complications. Often they contain large amount of nitrogen compounds in their composition in the form of amines, amides, heterocyclic compounds etc. The main products of their combustion are nitrogen oxides which emission can reach up to 2500 mg/m^3 [1]. Those oxides can be created during incineration from atmospheric and fuel-nitrogen via thermal, *prompt* or/and fuel nitrogen mechanisms [2-11]. In combustion zone, nitrogen is present transiently in the radicals HCN, CN, HNO and NH_i which transformations in this area lead to nitrogen oxides creation [4]. The fact is, that maintaining temperature above 900ºC in the freeboard zone of fluidized bed reactor, causes that NO emission is significantly higher than emission of N_2O and NO_2 [12].

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Reactions of nitrogen oxidation, especially fuel-nitrogen, are complex homogeneous, heterogeneous or catalytic processes, what causes that researches on them are carried on all over the world [13-20]. In the initial stage of nitrogen oxides creation from fuel nitrogen, during coal combustion HCN is produced. This particle is one of the main intermediate products of nitrogen oxidation, no matter how complex the conversion process occurs. It is also a product of decomposition of the amines in the initial phase of the process and its further reactions lead to the formation of nitrogen oxides N_xO_y. However, complex composition and structure of solid fuels (biomass, wastes) and specific hydrodynamic and temperature conditions in a fluidized bed cause that a detailed course of their combustion is not fully known. The goal of presented researches is to get knowledge about issue of conversion of fuel nitrogen into nitrogen oxides. Complexity of solid fuels combustion process caused, that as the first phase of researches combustion of propane with the addition of controlled amounts of diethylamine was carried out. Amine (N-compound) was dosed into the reaction zone in such amounts, which can be indicated in solid fuels.

Material and methods

Experimental researches were run in the laboratory scale, atmospheric fluidized bed reactor, which was applied during previous experiments of combustion processes [3]. The reactor was equipped with a system for supplying fuel, gaseous and liquid mixtures such as diethylamine.

The material of the bed, within all experiments, was chemically active calcium oxide which particles size was from the range 0.5-0.6 mm, its weight was about 350 g and its static height in reactor was approximately 41 mm but in dynamic conditions (temperature ~1000ºC) height was increasing to approx. 100 mm.

The fluidized bed had a temperature control system consisting of a movable radiation shield and blower of a cold air.

In aim of control of combustion processes and its further detailed analysis temperature, exhaust fumes composition and dynamic phenomena were registered during whole experiments. The temperature in the fluidized bed was measured by a set of eight uncovered thermocouples mounted in the reactor axis, at distances from 5 to 70 mm above the distributor in parallel with measurements run by two sheathed thermocouples which joints were permanently mounted 20 and 50 mm above gas distributor. Dynamic phenomena occurred during combustion were analyzed on the basis of the registered dynamic pressure changes. Registration was carried out using a difference pressure sensor mounted under gas distributor and by the microphone which was located about 550 mm above the surface of the bed. Measurements and recordings of exhaust fumes composition were carried out using analytical equipment: total organic compounds analyzer equipped with flame ionization detector (JUM® Model 3-200); O_2, CO, NO, NO_2, SO_2 analyzer equipped with electrochemical detectors (ECOM® SG Plus); O_2, CO, CO_2, SO_2 NO_x, N_2O analyzer equipped with electrochemical, nondispersive IR and chemiluminescence detectors (Horiba® PG250); FTIR analyzer equipped with Fourier transform IR detectors (Gasmet® DX-4000); O_2, CO, NO, NO_2, SO_2, CH_4, CO_2 analyzer equipped with electrochemical, nondispersive IR detectors (MRU® Vario Plus).

In the series of combustion experiments, propane was incinerated in fluidized bed reactor with as well as without addition of diethylamine. The series when only propane was present in reaction zone were carried out to get comparative data to the main part of the process. Diethylamine conversion and influence of amine compound presence in the reaction zone, as well as application of its different quantities to the reactor, on the conditions of fluidized bed combustion were analyzed. All experiments were carried out similar way. First stage was fluidization of the bed by air (rate of flow 1.66 dm^3/s) at ambient temperature. Next step was starting up of diethylamine dosage to the reactor, rate of flow was maintained constant during one single experiment, whereas in subsequent experiments different amounts of $(C_2H_5)_2NH$ were dosed (chosen rate of flows ensured respectively concentrations of amine approx. 900, 1800 and 3250 ppm in fuel-air mixture). Third stage was initiation of propane dosing into the reactor (rate of flow ~0.043 dm^3/s), which resulted in the creation of such fuel-air mixture composition, that the air-fuel ratio - λ_{bed} - was about 1.4. Start of propane addition was equivalent with ignition and beginning of combustion process. In a subsequent step incineration was carried out in a manner to obtain a gradual increase in bed temperature from ambient temperature to about 1000ºC and after receiving it, cooling of the reactor with outside air stream, to lower the temperature of the bed, was run. In experiments without addition of diethylamine to propane, only the step with dosage of this compound to the reactor was omitted.

Results and discussion

Changes of location of reaction zone in a fluidized bed as well as dynamic pressure and associated with those changes of chemical reactions mechanisms, depended strongly on temperature in combustion area. Additionally composition of flue gases depended strongly on temperature and whether diethylamine was or was not added to the reaction zone. To get knowledge about presented combustion processes, analysis of those parameters, as a function of the average bed temperature (mean arithmetic of four temperature measured by the thermocouples located from 10 to 30 mm above the distributor) was done.

Incineration under low bed temperature ~400ºC, was carried on above the bed (higher than 60 mm above the gas distributor) (Fig. 1a). Further increasing of the average bed temperature caused increase of the volume of gas flowing through the bed, what resulted in increase of the bed height. After exceeding the temperature above about 500ºC, the highest temperature measured in bed was located at surface of the bed (combustion was taking place at this location). Under average temperature above 600ºC combustion process runs mainly in the bed (Fig. 1a). In parallel to changes of bed height, changes of location of combustion zone with average temperature in fluidized bed were observed (Fig. 1a). Combustion of only gaseous fuels with air, as well as with addition to this mixture of diethylamine, led to movement of the maximum temperature location in the bed (zone of the most intense exothermic reaction) downwards, toward the gas distributor with increasing of average temperature (Fig. 1a). When average temperature in the bed was above 840ºC, combustion took place mainly in the area from 12 to 29 mm above the distributor (Fig. 1a), because autoignition in bubbles occurred during the shorter time that was necessary to pass their way through the bed. It was conclude that during combustion of propane with addition of diethylamine (1800 or 3250 ppm), area of the most intense reactions was moving faster towards distributor (Fig. 1a).

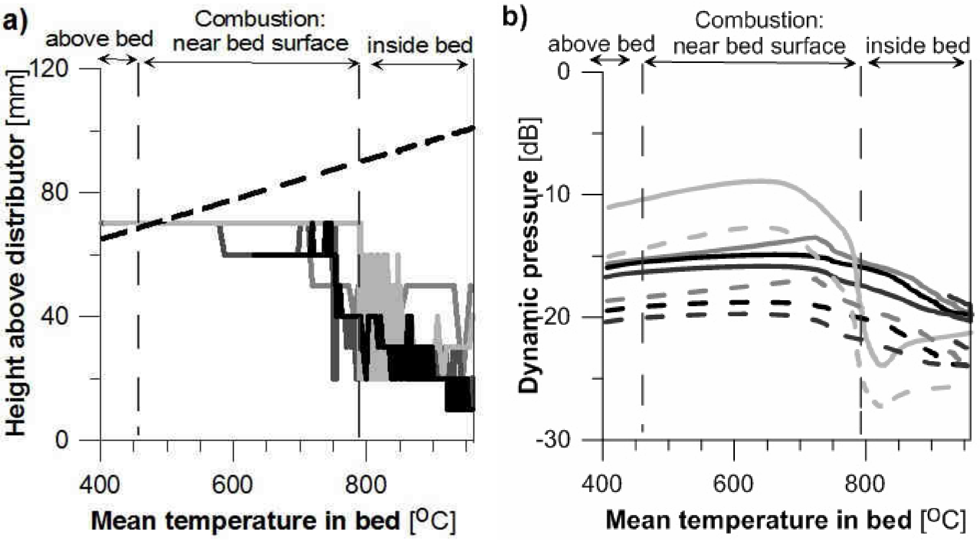

Fig. 1. Changes of chosen parameters of propane combustion processes with and without addition of diethylamine: a) height of the fluidized bed (▬ ▬) and the maximum temperature location during process (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) dynamic pressure registered by microphone (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm) and pressure difference sensor (amount of diethylamine addition to propane: ▬ ▬ - 0 ppm; ▬ ▬ - 900 ppm; ▬ ▬ - 1800 ppm; ▬ ▬ - 3250 ppm)

Registered dynamism pressure provided information about changes of the process dynamics related with increase of the temperature [21, 22]. When the temperature in the fluidized bed was relatively low (lower than 500ºC), signal amplitude in all analyzed experiments was low, what was result of continuous manner of combustion in flame (Fig. 1b). With the temperature increase, combustion on the bed surface was initiated. That was related with the change of the combustion mechanism into periodic, explosive combustion in large bubbles, what resulted in an increase of registered acoustic pressure. Within the temperature of about 700ºC dynamics of acoustic signals reached the maximum level. Further increasing of temperature resulted in the movement of process deeper into the bed. Bubbles with gases exploding inside them became less noisy and the energy released during the explosions was smaller what caused together, with occurrence of high bed layer located over the area of reaction, that registered acoustic effects were lower (Fig. 1b). Changes in the dynamic pressure recorded by microphone and by difference pressure sensor were similar in all experiments where diethylamine was added to the propane (Fig. 1b). Different situation took place when only propane was incinerated. In this case dynamic pressure (under the temperature lower than 800ºC) was noticeably higher than in the case of propane combustion with diethylamine. On the other hand, within combustion in the bed (temperature higher than 800ºC) acoustic signal amplitude in this case was lower (Fig. 1b). This can suggests that the kinetics of propane combustion without and with diethylamine addition is not completely similar. These phenomena could be a result of amine influence on the rate of combustion reactions (change of activation energy of particular reactions) which occurred in bubbles. Radicals which were products of amine conversion in reaction zone, caused that reaction with propane took place faster and bubbles during explosion contained smaller amount of fuel than in the case where only propane was incinerated. That could be a cause of registration of higher dynamic pressure when only propane was combusted, because explosions were more violent.

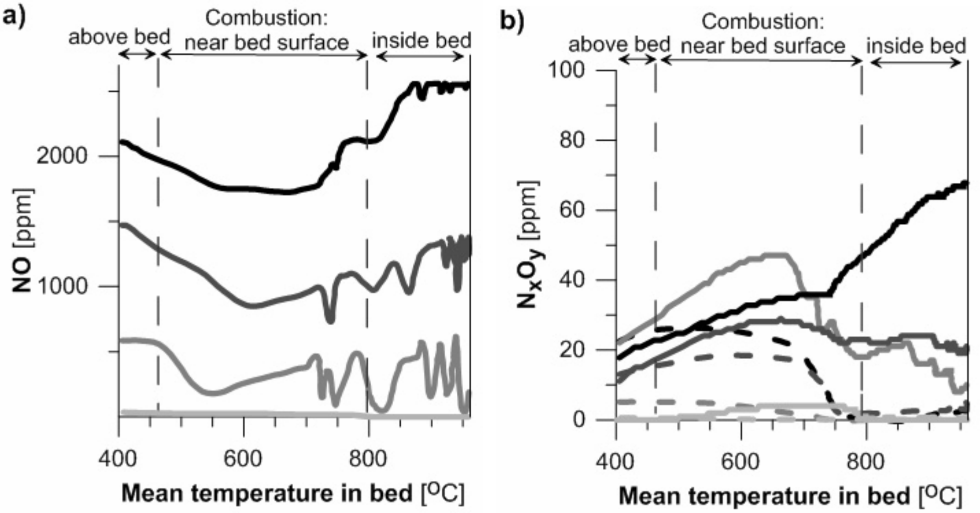

Fig. 2. Changes of nitrogen oxides concentration in flue gases as a function of mean bed temperature: a) nitric oxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) nitrous oxide (amount of diethylamine addition to propane: ▬ ▬ - 0 ppm; ▬ ▬ - 900 ppm; ▬ ▬ - 1800 ppm; ▬ ▬ - 3250 ppm) and nitrogen dioxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm)

The main products of diethylamine conversion, during combustion process, were nitrogen oxides. When amine was not dosed into the reaction zone, concentration of nitric oxide (the major oxide formed mostly by the *prompt* mechanism during combustion of hydrocarbon fuels in fluidized bed [2]) in the exhaust fumes did not exceed 30 ppm. Nitrogen dioxide concentration was 3-4 ppm and nitrous oxide concentration was lower than the gas detector sensivity (Fig. 2b). In the series of experiments where diethylamine was dosed into reaction zone, concentration of N_xO_y in exhaust fumes was relatively higher. The efficiency of amine conversion into N_xO_y during combustion was up to 78% and was higher when greater amounts of $(C_2H_5)_2NH$ were dosed into reaction zone. The main product of these reactions was, as mentioned before, nitric oxide which constituted more than 95% of the total created nitrogen oxides (Fig. 2a, b). Except N_xO_y no other compounds containing nitrogen in their structure were detected, therefore it was assumed that nitrogen is the only other product of diethylamine conversion. Initiation of amine oxidation process caused that concentration of NO in flue gases reached maximum value 2530, 1350, 580 ppm, when amine was dosed to the bed in respective amounts of 3250, 1800 and 900 ppm, under temperature higher than 900ºC (Fig. 2a). Concentrations of NO_2 and N_2O did not exceed respectively 70 and 30 ppm, when the highest amount of diethylamine was added to the reaction zone (Fig. 2b).

Analysis of efficiency of NO formation from diethylamine as a function of temperature revealed, that its maximum concentration occurred within the highest temperature. When only propane was incinerated, concentration of NO decreased with increase of temperature. Observed, different changes of nitric oxides concentrations with temperature in case of propane combustion with and without amine, cause necessity of further detailed analysis of these phenomena, because formation of NO in these both cases run under different kinetics.

In all experiments the amount of carbon monoxide in the exhaust fumes was increasing sharply with temperature increase and reached the maximum value at about 750ºC (Fig. 3a). This was a result of the inhibitory effect of bed, not hot enough, on the oxidation of CO to CO_2. Further increase of temperature caused a rapid decrease of CO concentration in the exhaust fumes (Fig. 3a). Addition of amine into reaction zone caused, that the highest CO concentration in flue gases was about half lower in comparison to experiment when no $(C_2H_5)_2NH$ was added to the propane (Fig. 3a).

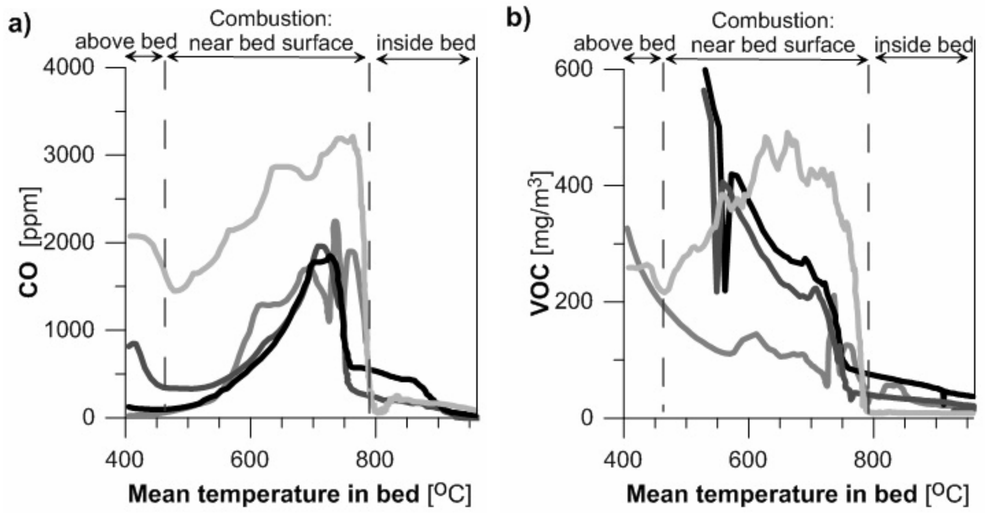

Fig. 3. Changes of chosen compounds concentration in flue gases as a function of mean bed temperature: a) carbon monoxide (amount of diethylamine addition to propane: ▬ - 0 ppm; ▬ - 900 ppm; ▬ - 1800 ppm; ▬ - 3250 ppm); b) volatile organic compounds (amount of diethylamine addition to propane as in Figure a)

The highest concentration of volatile organic compounds in the exhaust fumes was about 480 mg/m^3, in the case when propane was incinerated alone within the bed temperature 650ºC. In all experiments, obtainment of temperature higher than 800ºC caused rapid decrease of VOC concentration in exhaust fumes (Fig. 3b). In experiments with the application of diethylamine, the maximum VOC concentration was significantly lower within temperature range 620-750°C, than for experiment where only propane was incinerated. Similarly to the case of carbon monoxide reactions, addition of diethylamine to reaction zone influenced on VOC oxidization reactions.

On the basis of observed phenomena, it can be surmised that radicals, which were the intermediate products of diethylamine conversion, were involved in the reactions of CO and VOC oxidation.

Conclusions

Diethylamine, added to the propane during combustion in fluidized bed, was converted into N_xO_y up to 78% and residual amine was converted into nitrogen. The degree of conversion into N_xO_y was higher when greater amount of amine was dosed into reaction zone. The main formed nitrogen oxide was nitric oxide (more than 95%).

Radicals which were products of diethylamine conversion, present in the reaction zone, influenced on reactions involving CO and VOCs. They affected the acceleration of oxidization processes. The degree of CO and VOCs conversion was at high level even by temperature lower than 800°C, when the combustion took place yet near bed surface.

During combustion, N_2O was detected in flue gases at a level not exceeding 30 ppm.

Effect of diethylamine on the kinetics of propane combustion process is noticeable but limited. It can therefore be assumed that amine impact will also be noticeable during the combustion of alternative fuels with high fuel-nitrogen content. Amines are in fact one of the major compounds which are source of bounded nitrogen in fuels. Their further reactions lead to the formation of nitrogen oxides.

Acknowledgments

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KONWERSJA DIETYLOAMINY DO TLENKÓW AZOTU PODCZAS SPALANIA W AKTYWNYM CHEMICZNIE ZŁOŻU FLUIDALNYM

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Abstrakt: Przeprowadzono i przeanalizowano procesy spalania paliwa gazowego (propanu) bez oraz z dodatkiem różnych ilości dietyloaminy, w złożu fluidalnym zbudowanym z chemicznie aktywnego tlenku wapnia. Na podstawie temperatury, ciśnienia dynamicznego w strefie reakcji oraz składu spalin dokonano analizy procesów konwersji dietyloaminy do tlenków azotu i jej wpływu na kinetykę procesu spalania propanu. Złożoność procesu spalania paliw stałych (alternatywnych lub biomasy, które mogą zawierać wysoką ilość związków azotu w postaci amin, związków heterocyklicznych, aminokwasów itp.) spowodowała, że na tym etapie badań zdecydowano się na przeprowadzenie spalania paliwa gazowego. Aminę dozowano do strefy reakcyjnej w takich ilościach (około: 900, 1800, 3250 ppm), które mogłyby dawać stężenia tlenków azotu w spalinach podobne do rejestrowanych podczas spalania paliw alternatywnych o dużej zawartości azotu. Wyniki badań wykazały, że do 78% związku azotowego ulegało konwersji do N_xO_y. Stopień konwersji był większy, gdy większe ilości $(C_2H_5)_2NH$ dozowano do strefy reakcji. Głównym tlenkiem azotu utworzonym podczas spalania był tlenek azotu(II), który stanowił ponad 95% całkowitej ilości N_xO_y. Pozostała amina była przekształcana do azotu. Stwierdzono zauważalny, ale ograniczony wpływ $(C_2H_5)_2NH$ na kinetykę procesu spalania propanu. Dietyloamina i produkty jej konwersji, takie jak rodniki obecne w strefie spalania, wpływały na reakcje utleniania tlenku węgla i lotnych związków organicznych.

Słowa kluczowe: emisja tlenków azotu, spalenie w złożu fluidalnym, spalanie paliw alternatywnych, spalanie biomasy

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PHOTOCATALYTIC HYDROGEN PRODUCTION FROM GLYCEROL - PRELIMINARY STUDY USING Pt/TiO_2 AND Pd/TiO_2 AS CATALYSTS

FOTOKATALITYCZNA PRODUKCJA WODORU Z GLICERYNY - BADANIA WSTĘPNE Z WYKORZYSTANIEM Pt/TiO_2 ORAZ Pd/TiO_2 JAKO KATALIZATORÓW

Abstract: Concern for the environment and the use of renewable energy sources are the two main priorities of energy policy combined with the environmental policy based on the principles of sustainable development. Many aspects should be taken into account in the case of energy production based on biomass/biofuels, in particular the possibility of additional by-products formation. When it comes to biodiesel production, the formation of huge amounts of surplus crude glycerol may be such a problem. The well-known, traditional methods of glycerol utilization are ineffective, which was proved by the big price drop in the glycerol market. High hopes to solve this problem are placed in new technologies: bio-conversion of glycerol to various chemicals or energy carriers and photocatalytic conversion to hydrogen. The paper presents the results of some preliminary studies of photocatalytic glycerol conversion to hydrogen. The investigation was focused on proper selection of catalysts and on the search for the optimum conditions of the photocatalytic process using TiO_2 doped with platinum or palladium (0.1, 0.5, 1 wt.%). The initial glycerol concentration in the solution was 4.5%. Photocatalysts were obtained by the sol-gel method. The effect of irradiation intensity was achieved by using 2-4 xenon lamps, the power of 75 W each. Gas product was analyzed by gas chromatography. The highest efficiency of hydrogen production (19.33 mmol/g of catalyst·h) was obtained for Pt doped TiO_2. The production rate of hydrogen depended on catalyst concentration, the amount of the noble metal in the catalysts, the concentration of glycerol in the solution and the intensity of irradiation.

Keywords: glycerol, hydrogen, photocatalysis

Introduction

Biodiesel is produced by transesterification of vegetable oils [1, 2]. The increase of biodiesel production observed all around the world contributes to the surplus of glycerol on the market. Therefore, nowadays, much emphasis is placed on the development of new technologies of glycerol utilization. Unfortunately, effective utilization of large amounts of waste fractions creates serious economic and technological problems [2]. One of the most promising processes seems to be its photocatalytic conversion into hydrogen, which is considered to be a modern and environmentally friendly method. The idea to apply this method emerged from the previous studies on the degradation of other organic pollutants

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(*eg* alcohols) into hydrogen. Photoconversion of glycerol is described by the below reaction [3, 4]:

$$C_3H_8O_{3(\text{liquid})} + 3H_2O_{(\text{liquid})} \xrightarrow[hv]{\text{cat.}TiO_2} 7H_{2(\text{gas})} + 3CO_{2(\text{gas})} \tag{1}$$

Photocatalysis is based on the absorption of light by the catalyst or by the substrate. Photoexcitation of the catalyst is based on the transfer of an electron from the valence band to the conduction band after it has absorbed an adequate portion of radiant energy. As a result of the process, we obtained one electron with reduction properties in the conduction band and a hole with oxidation properties in the valence band [1, 2, 5].

Photocatalytic conversion of glycerol to hydrogen is a promising way to convert solar energy into chemical energy [1, 5]. Titanium dioxide (TiO_2) is the most frequently used catalyst for the conversion of organic compounds (pollutants or wastes - including glycerol) into hydrogen. Surface modification of TiO_2 leads to the reduction in the band-gap energy and produces catalysts, which are active in the visible light and UV. Photocatalysts (*eg* TiO_2) that should be active over the entire visible spectrum are obtained by doping with nonmetals (N, S, C, B, P, F, I) and adding noble metals (or other metals) [4, 5]. The benefits of using TiO_2 as a basic support are its chemical and photochemical stability, low cost and non-toxicity [1, 5].

The aim was to test the catalysts (based on TiO_2) that were doped with Pt or Pd in the process of photoconversion of glycerol to hydrogen.

Materials and methods

Chemicals

Titanium(IV) isopropoxide (TIP) (97%) was purchased from Aldrich Chem. and used as the source of titanium for the preparation of TiO_2 nanoparticles. A commercial form of TiO_2 (P25, crystalline composition: 80% anatase, 20% rutile, surface area 50 g/m^2) was purchased from Evonik, Germany. 99.9% chloroplatinic acid hydrate ($H_2PtCl_6 \cdot xH_2O$), 5 wt.% solution in 10 wt.% HCl palladium(II) chloride ($PdCl_2$) were provided by Aldrich Chem.

Experimental procedure

Reactions were carried out in a semi-batch quartz reactor (the volume of 40 cm^3). The reactor was charged with the mixture of glycerol aqueous solution (15 cm^3). The reaction mixture containing glycerol, water and catalyst was irradiated using xenon lamps (4 lamps Xe-arc XBO 75 W each), (4.5 wt.%) and photocatalysts - Pt/TiO_2 or Pd/TiO_2 (70 mg). Characteristics of photocatalyst are shown in Table 1. The temperature of the reaction mixture was in the range of 40-55°C. Argon was used as a carrier gas, at the flow rate of 30 cm^3/min, to remove air from the reactor before the start of the reaction, to mix the liquid and to remove gas products from the reactor when performing the process. The almost homogeneous slurry of the catalyst was obtained by magnetic stirring and the flow of argon through a special distributor. Each of the experiments lasted approximately

4-6 hours. Gaseous phase was analyzed every 15 minutes. The scheme of laboratory set-up is presented in Figure 1.

Table 1

Photocatalysts characteristics for photoconversion of glycerol

Photocatalyst type	**Preparation method**	**The type of metal precursor**	**Content of metal precursor [wt.%]**	**BET surface area [m^2/g]**
0.1 Pt	sol-gel	$H_2Cl_6PtxH_2O$	0.1	92
0.5 Pt		$H_2Cl_6PtxH_2O$	0.5	148
1 Pt		$H_2Cl_6PtxH_2O$	1	130
0.1 Pd		$PdCl_2$	0.1	126
0.5 Pd		$PdCl_2$	0.5	86
1 Pd		$PdCl_2$	1	81

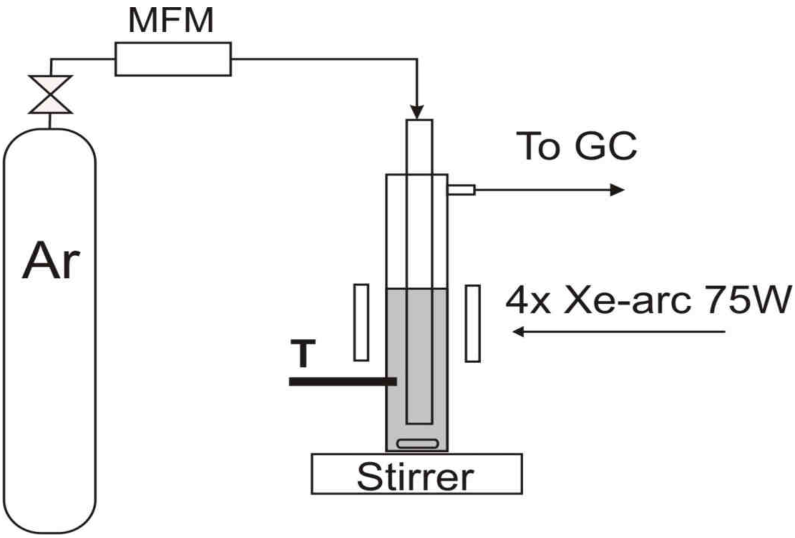

Fig. 1. The layout of laboratory set-up (Ar - inert gas; GC - the gas chromatograph; magnetic stirrer - 500 rpm)

Results and discussion

The main goal of the part of the study presented in this article was to compare the efficiency of hydrogen production for the two catalysts in the experiments carried out under the same conditions. Each time the amount of catalyst added to the solution was 70 mg. The volume of glycerol in water solution at the concentration of 4.5 wt.% was equal to 15 cm^3. Two types of catalysts were used in the experiments - TiO_2 doped with platinum or the second TiO_2 doped with palladium. In both cases the amount of the above metals in the TiO_2 was the same, respectively 0.1 and 0.5 representing 1% by weight. In each experiment we used four xenon lamps, the power of 75 W each. Operational conditions for each experiment are shown in Table 2. The comparison of hydrogen production efficiencies obtained in the experiments is presented in Figures 2 and 3.

Table 2

Experimental conditions and efficiency of glycerol photoconversion

Photocatalyst type	**Photocatalyst amount [mg]**	**Glycerol initial concentration [wt.%]**	**Irradiation time [min]**	**Power of the light source [W]**	**Average hydrogen productivity [mmol/g_{cat} h]**
0.1 Pt	70	4.5	180	300	17.35
0.5 Pt			210		11.18
1 Pt			195		6.12
0.1 Pd			150		13.41
0.5 Pd			180		6.20
1 Pd			180		1.41

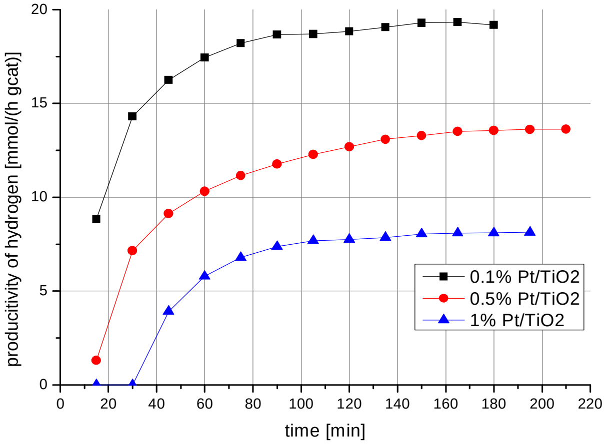

Fig. 2. Efficiency of hydrogen production during irradiation of aqueous glycerol solution in the presence of photocatalyst obtained by sol-gel method depending on the TiO_2 doped with Pt (0.1, 0.5, 1 wt.%)

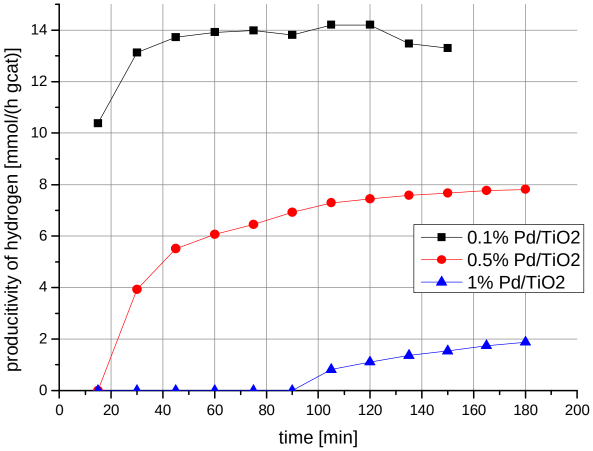

Fig. 3. Efficiency of hydrogen production during the irradiation of aqueous glycerol solution in the presence of photocatalyst obtained by sol-gel method depending on the TiO_2 doped with Pd (0.1, 0.5, 1 wt.%)

Hydrogen production yield obtained for Pt catalyst was higher than for Pd (catalysts prepared by the sol-gel method and photodeposition). The lower metal dopant content, the higher the efficiency of hydrogen production. The most optimal process conditions offering the highest H_2 productivity were found for 4.5 wt.% of glycerol concentration of aqueous solution and 0.07 g of the catalyst weight. The highest production efficiency of hydrogen for the 0.1% Pt (TiO_2) catalyst prepared by sol-gel for 4.5% glycerol solution was found to be 19.33 mmol/g_{cat} h. Hydrogen was identified in all the studied samples while carbon dioxide was not detected.

Conclusions

Results of the present study show that the highest efficiency of hydrogen production was achieved for the catalyst Pt(TiO_2) rather than for Pd/TiO_2. Generation of hydrogen largely depends on the content of dopant metal and on the type of the catalyst.

Acknowledgments

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FOTOKATALITYCZNA PRODUKCJA WODORU Z GLICERYNY - BADANIA WSTĘPNE Z WYKORZYSTANIEM Pt/TiO_2 ORAZ Pd/TiO_2 JAKO KATALIZATORÓW

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Abstrakt: Efektywna produkcja energii oparta na biomasie/biopaliwach powinna uwzględniać wiele aspektów, w szczególności możliwość powstania dodatkowych produktów ubocznych. W przypadku produkcji biodiesla takim problemem może być zagospodarowanie dużych ilości odpadowej gliceryny powstającej w tym procesie. Dotychczas stosowane tradycyjne metody jej utylizacji okazują się nieefektywne, o czym świadczy duży spadek cen na rynku surowej gliceryny. Duże nadzieje jej korzystnego zagospodarowania wiązane są z nowymi technologiami - biokonwersją do różnych produktów chemicznych i energetycznych oraz fotokatalityczną konwersją do wodoru. W pracy przedstawiono badania przeprowadzone w celu selekcji katalizatorów, które mogą być wykorzystane do konwersji gliceryny, oraz znalezienia optymalnych warunków procesowych. Rozkład gliceryny badano, stosując jako katalizator TiO_2 domieszkowany platyną lub palladem (0,1, 0,5, 1% wag.). Stężenie gliceryny w roztworze wynosiło 4,5%. Fotokatalizatory otrzymano metodą zol-żel. Jako źródło światła wykorzystano od 2 do 4 lamp ksenonowych o mocy 75 W. Produkt gazowy analizowano metodą chromatografii gazowej. Najwyższą wydajność produkcji wodoru (19,33 mmola/g kat·h) otrzymano dla fotokatalizatora TiO_2 domieszkowanego 0,5% Pt. Efektywność generowania wodoru zależy od rodzaju katalizatora, jego stężenia w roztworze, zawartości metalu szlachetnego w katalizatorze, stężenia gliceryny oraz intensywności naświetlania.

Słowa kluczowe: gliceryna, wodór, fotokataliza

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BIOACCUMULATIVE AND BIOINDICATIVE ROLE OF FUNGI IN THE ENVIRONMENT

BIOAKUMULACYJNA I BIOINDYKACYJNA ROLA GRZYBÓW W ŚRODOWISKU

Abstract: Mycelial construction of mushrooms is considered as a good biomass for heavy metals binding as well as lots of elements, including toxic and radioactive ones. Between various fungi known to bind heavy metals, mycelium of *Pleurotus* spp. can be used in Cd indication and accumulation, by means of fungal biomass. In this work possible role of *Pleurotus ostreatus* in accumulation of radionuclides is presented. This is important because this fungus is one of broadly cultivated mushrooms, and it can grow as saprobic organism on various substrates. Naturally occurring fruiting bodies of *P. ostreatus* were used in studies as a potential marker of atmospheric radioactive pollution. The samples of fruiting bodies in different age (young, mature and old) were collected in the center of Opole. Measurements of the gamma radionuclides activity concentration in dried samples were carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution. Potassium concentration in fruiting bodies was similar in each sample, though it was the lowest in the young specimen. Activity concentration of Cs-137 was also related with the age of the mushroom. The biggest concentration was determined in old specimen, while in the young and mature ones it was similar. In the mature and old mushrooms activity concentration of Pb-210 was lower than minimum detectable activity. Pb-212 was determined only in fruiting bodies of old specimen.

Keywords: mushrooms, radionuclides, environmental pollution indication

Introduction

Mushrooms are investigated as a source of numerous elements and, among them, also these classified as toxic and radioactive [1, 2].

Pleurotus ostreatus is one of broadly cultivated mushrooms as well as it can grow as saprotrophic organism on various substrates, f. ex. trunks. One of most frequently cultivated is an oyster mushroom (*Pleurotus osteratus*). An oyster mushroom is cultivated for not long time, the first information about its cultivation becomes from 1917, but before it was collected in natural environment, also naturally infected trunks were collected and stored in wet conditions waiting for fructification. The first scientific name of oyster mushroom was *Agaricus ostreatus*, nowadays the number of 36 species were described in the genera of *Pleurotus*. The genera *Pleurotus* is classified in the phylum *Basidiomycota.* Mycelium of basidiomycetous fungi is characterized by clump connections occurring on vegetative hypha (Fig. 1), which is a typical hallmark for this kind of mushrooms, as well as for genus *Pleurotus*. Only two species of *Pleurotus* are not edible, and 25 of them are cultivated broadly in the world. Between cultivated mushrooms the genera of *Pleurotus* has the biggest number of cultivated species and cultivars. In central Europe an oyster mushroom can grow saprotrophically on the dead or living trunks of deciduous trees and

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naturally on the ground. Fruiting bodies occur in November and December. Naturally occurred mycelium grows saprotrophically and do not need many nutritional requirements [3]. This makes it easy in cultivation on various lignin and cellulose substrates and wastes. Fruiting bodies of oyster mushroom grow in big groups consisted of bigger or smaller ones, on the same base [4]. They are a good source of mineral substances. There were found 3 g of potassium, 150 mg of calcium and 125-757 mg of sodium in 100 g of dry mass of fruiting bodies of oyster mushroom [5]. They contain also trace amounts of iodine, fluorine, copper, zinc, mercury and manganese [6, 7]. Mushrooms can collect also lots of elements including the toxic and the radioactive ones. Mushrooms or single mycelia are considered as good biomass for binding heavy metals. Between various fungi known to bind heavy metals, mycelium of *Pleurotus sajor-caju* can be used to remove Cd by means of fungal biomass [8].

In our work the naturally occurring *P. ostreatus* fruiting bodies were used as a potential marker of atmospheric radioactive pollution.

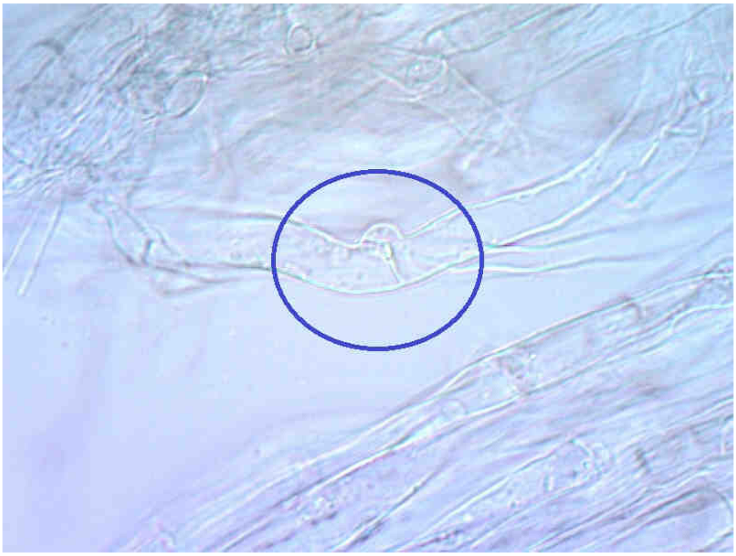

Fig. 1. Hyphae of *P. ostreatus* with a clump connection (marked in the ring) (photo by E. Moliszewska)

Materials and methods

The samples of *P. ostreatus* fruiting bodies were collected from the trunk of living lime-tree (*Tilia cordata*) growing on the side of the average traffic road in the center of Opole. They were collected during two winter seasons: the end of November (2012), the end of December (2013) and the end of February (2014). Additionally the age of the fruiting bodies was qualified as young specimens (Fig. 2), mature (Fig. 3) and old specimens. For determination of the gamma radionuclides activity dried samples of fungi fruiting body were prepared. Samples were oven dried in 105°C since the mass of the sample was stable and then dried by mortar.

Fig. 2. Young fruiting bodies of *P. ostreatus* (photo by E. Moliszewska)

The measurement of radionuclide activity in fungal samples was carried out by means of a gamma-spectrometer with a germanium detector HPGe (Canberra) of high resolution: 1.29 keV (FWHM) at 662 and 1.70 keV (FWHM) at 1332 keV. Relative efficiency: 21.7%. Energy and efficiency calibration of the gamma spectrometer was performed with the standard solutions type MBSS 2 (Czech Metrological Institute, Praha), which covers an energy range from 59.54 to 1836.06 keV. The geometry of the calibration source was a Marinelli container (447.7 ±4.5 cm^3), with density 0.99 ±0.01 g/cm^3, containing Am-241, Cd-109, Ce-139, Co-57, Co-60, Cs-137, Sn-113, Sr-85, Y-88 and Hg-203. The geometry of sample container was a similar Marinelli of 450 cm^3. Time of measurement was 24 h for all samples. Measuring process and analysis of spectra were computer controlled with the use of software GENIE 2000.

Some radionuclides were determined in each sample, and some of them appeared in determinable concentrations only in single samples. Results were shown as the activity concentrations of radionuclides (a), and the measurements uncertainties (Δa). The values lower than minimum detectable activity (MDA) are marked with < MDA.

Fig. 3. Mature fruiting bodies of *P. ostreatus* (photo by E. Moliszewska)

Results

The following radioisotopes were determined in fruiting bodies of *P. ostreatus* samples: Pb-212 (thorium decay chain), Pb-210 (radium decay chain), K-40 and artificial Cs-137. In Table 1 the half-life times of the determined radioisotopes are shown. Among the radioisotopes determined in fungal samples, K-40 is the most stable.

Table 1

Half-life times of the radioisotopes determined in soil samples

Pb-212	**Pb-210**	**K-40**	**Cs-137**
10.64 h	22.2 a	$1.25 \cdot 10^9$ a	30.1 a

It was observed that K-40 concentrations in fruiting bodies of *P. ostreatus* were similar to each other, though it was the lowest in the young specimen (Table 2). The Cs-137 is present in environment and it is also determined in the investigated mushroom samples. Both, direct atmospheric deposition on the surface and transport from background via mycelium, could deliver Cs-137 to the fruiting bodies. Activity concentration of this radioisotope was also related with the age of the mushroom. The biggest concentration was determined in old specimen, while in the young and mature ones it was similar (Table 2).

The Pb-210 radioisotope was found in young mushrooms (Table 2), though the measurement uncertainty was significant. In the mature and old mushrooms activity concentration of Pb-210 was lower than MDA.

The Pb-212 isotope was determined only in old mushrooms at the level 1.27 Bq/kg (Table 2).

Table 2

The gamma radionuclides activity in dried samples of fruiting bodies

Time (age)	$a_{K\text{-}40}$ **[kBq/kg]**	$\Delta a_{K\text{-}40}$ **[kBq/kg]**	$a_{Cs\text{-}137}$ **[Bq/kg]**	$\Delta a_{Cs\text{-}137}$ **[Bq/kg]**	$a_{Pb\text{-}210}$ **[Bq/kg]**	$\Delta a_{Pb\text{-}210}$ **[Bq/kg]**	$a_{Pb\text{-}212}$ **[Bq/kg]**	$\Delta a_{Pb\text{-}212}$ **[Bq/kg]**
November 2012 (mature)	1.059	0.040	4.76	0.64	< MDA	–	< MDA	–
December 2013 (young)	0.941	0.039	5.30	0.75	45.2	44.9	< MDA	–
February 2014 (old)	1.050	0.033	10.08	0.46	< MDA	–	1.27	0.28

Discussion

Biosorption is an area of increasing biotechnological interests. Especially since the removal processes of potentially toxic and/or valuable metals and radionuclides from contaminated sources can be used to detoxify them prior to environmental elimination [9]. Mushrooms may accumulate great concentrations of metals. Some of them are involved in fungal growth, metabolism and differentiation (*eg* K, Na, Mg, Ca, Mn, Fe, Cu, Zn, Co and Ni), while others, *eg* Rb, Cs, Al, Cd, Ag, Au, Hg and Pb have probably no essential functions. Some of them, such as mercury, cadmium, lead and copper can cause morphological abnormalities, reduce growth and increase mortality and mutagenic effects in humans [10, 11]. Yilmaz et al [12] found that fungal species growing on wood contain, in general, lower concentrations of heavy metals than fungi growing on soil. This observation is proper for cultivated mushrooms, but naturally occurring ones can grow on different, contaminated substrates, as *eg* fruiting bodies of tested in this research mushrooms. The source of contamination was mostly city traffic and precipitation, so consumption of such mushrooms as food may lead to intoxication. In this way selected food products may deliver to an average person certain doses of both natural and artificial radioactive isotopes [13].

The abundance of K-40 in potassium is constant and is 0.0119%. Because of the constant content, activity concentration of K-40 is the measure of the total potassium concentration. It seems that tested specimens do not collect continuously this element. Desorption of immobilized cesium cations is supported by the ones of similar size, like K^+ or NH_4^+. The Cs-137 and K-40 isotopes have similar chemical properties, but their origin in nature is different. In opposite to Cs-137, the K-40 radioisotope occurs naturally in environment.

The Cs-137 isotope is the artificial radionuclide, with half-life time of 30.1 years. Its circulation in environment started about 70 years ago. It was a product of a number of nuclear tests performed in 50. and 60. of 20th century [14]. Environment was contaminated also as a result of a number of incidental, uncontrolled releases, like, for example, accidents in Chernobyl (1986) and Fukushima Dai-Ichi (2011) nuclear power plants [15-17]. The Cs-137 is present in environment up to now, and it was also determined in the investigated mushroom samples. Probably growth of the fruiting bodies of *P. ostreatus* was associated with continuous intake of Cs-137 from surrounding area.

The Pb-210 radioisotope found in young mushrooms is the member of the natural uranium decay series. Is half-time time is 22.2 years, which is significantly longer than that for Pb-210 ancestors in decay series. It could be supposed that Pb-210 appeared primarily in mushroom and its presence is not a result of radioactive decay of its closest ancestors in decay series. It could be concluded that this isotope appeared in mushroom surrounding only in a period of time, at the beginning of fruiting bodies growth. Subsequent increase in mass of mushroom caused decrease in Pb-210 concentration and fall of activity concentration below MDA. In old mushrooms the Pb-212 isotope was determined (Table 2). It is a member of the natural thorium decay series. Its half-life time is not long (only 10.6 h). It possible source is Th-228 with half-life time 1.9 years. Occurrence of Pb-212 in fruiting bodies of old specimen supposed deposition of the radioisotope from atmosphere or migration from background. This process was slower than increases in mass of the mushroom. Bishnoi and Garima [18] observed that biosorption of metal ions increase during the lag period or early stages of growth and declines as cultures reached stationary phase (for *Aspergillus niger, Penicillium spinulosum, Trichoderma viride*). The age of fruiting body or its size, are of less importance. Some authors reported higher metal concentrations in younger fruiting bodies. This is explained by the transport of a metal from mycelium to the fruiting body during the start of fructification. During the following increase of the fruiting body mass, the metal concentration decreases. In general the proportion of metal concentrations from atmospheric depositions seems to be of less importance due to the short lifetime of a fruiting body of typical edible mushrooms, which is usually 10 ±14 days [19], but fruiting bodies of naturally occurring *P. ostreatus* can persist longer in their natural position.

Conclusions

Potassium concentration in fruiting bodies was similar in each sample, though it was the lowest in the young specimen. Activity concentration of Cs-137 was also related with the age of the mushroom. The biggest concentration was determined in old specimen, while in the young and mature ones it was similar. In the mature and old mushrooms activity concentration of Pb-210 was lower than minimum detectable activity. Pb-212 was determined only in fruiting bodies of old specimen.

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BIOAKUMULACYJNA I BIOINDYKACYJNA ROLA GRZYBÓW W ŚRODOWISKU

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Abstrakt: Grzybnia, szczególnie grzybów wielkoowocnikowych, dzięki zdolności do akumulowania metali ciężkich stanowi potencjalne źródło informacji o zanieczyszczeniu środowiska. Wśród nich należy wymienić boczniaka (*Pleurotus osteratus*), grzyba zarówno uprawnego, jak i występującego naturalnie. W pracy wykonano analizę zdolności bioindykacyjnych i biokumulacyjnych tego gatunku w stosunku do izotopów gamma-promieniotwórczych. Próbki *P. osteratus* w różnym wieku (młode, dojrzałe, starzejące) zebrano w naturalnym stanowisku, w centrum Opola. Aktywności izotopu K-40 były podobne we wszystkich badanych próbkach, przy czym najniższa koncentracja tego izotopu została stwierdzona w najmłodszych owocnikach. Izotop Cs-137 najliczniej występował w najstarszych owocnikach. Radioizotop Pb-210 znaleziono w młodych owocnikach, a izotop Pb-212 stwierdzono w starych owocnikach.

Słowa kluczowe: grzyby, radionuklidy, indykacja zanieczyszczeń środowiska

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DEWATERING OF SLUDGE FROM ELECTROPLATING WASTEWATER TREATMENT

ODWADNIALNOŚĆ OSADÓW POCHODZĄCYCH Z OCZYSZCZANIA ŚCIEKÓW GALWANICZNYCH

Abstract: Electroplating coating of products more sustainable coatings is their protection or decoration. As a result of these technological processes generated waste water, which are treatment. During the treatment of waste water produced sludge that were the subject of research. Sludge were from wastewater treatment plants located at the manufacturing plant which produces car parts. They were taken from the sludge tank, preceded by sedimentation in the lamella. In order to determine their sensitivity to dewatering the first step was selected the type and dose of reagent. In the second stage of the study conditioned sludge were tested mechanical dewatering centrifuge and belt press simulator. The results obtained showed that the most effective effect was observed when using anionic polyelectrolytes Praestol 2505 and Superfloc A 110 and A 130. Were used in a dose of 2.1 mg/g TS to 3.4 mg/g TS, and from 8.2 mg/g TS to 15.4 mg/g TS. The use of too low a dose of reagent and overdose resulted in unsatisfactory conditioning effects. The excess polyelectrolyte increased viscosity of the liquid sludge, which gave slower water contained therein. Conditioned selected polyelectrolytes sludge were subjected to a mechanical dewatering. The sludge obtained after centrifugation is characterized by a total solids a maximum of 12.7%. The centrifugation process efficiency was influenced by the spin speed and the duration of the process. The best results were obtained for a duration of 10 min and a speed of 3000 turns/min. A higher degree of dewatering of 29.5% TS obtained using the simulator of belt press.

Keywords: sludge from industrial, mechanical dewatering, the choice of polyelectrolyte

Introduction

Electroplating process is used to layer products with fewer precious materials with more durable layers. In connection with this operation surface of the unit achieves better corrosion and heat-resistant properties. In addition, galvanic coating of the products can be carried out for the improvement of surface protective and decorative purposes and to give the required characteristics of the profiled elements, mainly hardness and wear resistance (technical coating) [1-4]. Electroplating process consists of several stages. First, the devices are mechanically cleaned, degreased and acidified. The aim of the acidification is to remove oxides from the surface of objects created in the degreasing and etching of the surface cloudy. After preparatory operations galvanic coating process takes place. Electroplating is performed under the effect of direct electric current. The bath composition obviously depends on the kind of the cover. This may be a process of coating with nickel, chromium, copper, zinc plating, oxidation, blackening, cadmium, lead, etc. The final stage of treatment is aimed at upgrading and consolidating imposed electroplated coatings. For this purpose, the most commonly used is passivation, coloring, polishing and varnishing [1, 5, 6]. After completion of the electroplating bath items are subjected to washing. Flushing is normally carried out in tanks with a continuous flow of fresh water, rarely used rinse spray [7]. As a result wastewater is produced, *ie* backwash water and spent baths. In

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the diluted wastewater washing water generated in the process of chemical or electrochemical treatment of objects are present. Backwash water pollution are main components of the bath [1, 5, 6]. On the other hand, taking into account the type of impurities from the electroplating industry wastewater, wastewater from cleaning and degreasing, waste of digestion, waste chromium (water washing after the electrochemical plating and chromate passivation) and cyanide wastewater can be distinguished. This wastewater is treated and as a result of the process sludge is produced [1, 4-6, 8].

Subject and methodology of research

The aim of the subject was sludge from industrial wastewater treatment plant taking place next to the automotive manufacturing. System of technological wastewater treatment consists of: reduction of chromium(VI) using a sodium bisulfate (waste chrome), coagulation process with the use of Flokor 1A (for the waste water mixed, precipitation of by the addition of milk of lime solution. Then sedimentation process in lamella tank where separation of the treated sewage sludge. Sedimentation process is enhanced with polyelectrolyte conditioning. The separated sludge is periodically pumped into the sludge tank. Then adjustment of the pH by the use of H_2SO_4 or NaOH to obtain pH of fulfilling the requirements for wastewater that can be discharged into the drains. The final stage of wastewater treatment process is filtration through sand filter. This filter removes from wastewater remains of insoluble's.

The tests were performed for sludge taken from the tank. The tests were carried out in three stages. In the first stage of the analysis examined the sludge properties. The extent of the research included the like: total solids (TS), volatile solids (VS), specific resistance, capillary suction time (CST), pH, odor. All analyzes were conducted in accordance with the applicable standards [9-13]. In the second stage the type and dose of polyelectrolyte was select based on the flocculation tests, strength, CST. Conditioning with polyelectrolyte enables to change the structure of the sludge and the surface of the dispersed solid phase particles, which leads to reduction of the interface and reduce the force of binding water from the surface of sludge flocs. Cationic and anionic polyelectrolytes were used in conditioning process. They are presented in Table 1.

Table 1

Type of tested polyelectrolyte

An ordinal number	Polyelectrolyte	Ionic character
1	Praestol 644	weak cationic
2	Praestol 611	weak anionic
3	Praestol 2505	anionic
4	Zetag 63	cationic
5	Zetag 47	cationic
6	Magnafloc 155	anionic
7	Zetag 8846	cationic
8	Praestol 2640	average anionic
9	Praestol 2540	average anionic
10	Superfloc A 110	anionic
11	Superfloc A 150	anionic
12	Superfloc A 130	anionic

Flocculation test was based on visual assessment of the size and structure of the flocs after the introduction of the sludge and mixing. Then, based on the strength test flocs strength was evaluated. That flocs structure should be robust, due to the centrifuge action of the centrifugal force and the shearing forces occurring in the belt press. For this purpose, from the depth of 10 cm five times the sludge was poured from the beaker to beaker. Sieving test was carried out using Buchner funnel lined with filter belt. Filter belt was made of the same material as the belt filter used for mechanical dewatering. The flocculated sludge was placed on the belt and the filtrate was collected.

The dewatering tests sludge were carried out on the simulator belt press and in a centrifuge nn the last stage. In the study a laboratory centrifuge Centrifuge company MPW - type 340 with a maximum speed 4000 rev./min and time centrifugation of the 1 to 60 min were used. The sludge was conditioned by selected doses and type of polyelectrolyte. It was centrifuged for a period of 5 and 10 minute, whit velocity 1500 and 3000 rev./min. After centrifugation total solids were analyzed.

In turn, as the belt filter press simulator Büchner funnel lined with filter belt was used. It was made of the same material as the belt filter press used for mechanical dewatering, and piston pressure. In the initial stage of the dewatering gravity filtration takes place, wherein water is removed during the conditioning process. Then, the clarity and quantity filtrate obtained in 5 minutes were measured. During filtration it was checked whether cake sludge produced on the belt does not block the mesh. Then, shaking the funnel in horizontal position it was determined whether the sludge cake was broken and whether it was susceptible to create a sludge roller. Then, the sample of mechanical dewatering of sludge cake by means of the pressure piston was made. After dewatering total solids were measured.

Results and analysis

The results of physico-chemical sludge derived from the treatment of wastewater from the electroplating industry showed that the precipitate was characterized by a slightly alkaline pH equal to 8.63, and also had a characteristic smell and intense and characteristic grey - green color. The test sludge showed high hydration amounting to 98.6%, a low total solids (TS) 1.4% and volatile solids (VS) 15.7% TS. Low content of volatile solids indicates that it is a mineral sludge derived from the treatment of industrial waste water. Furthermore, the sludge tested showed good filtration properties, as evidenced by the short period of capillary suction time (CST) equal to 68 seconds and a low value of the specific resistance equal to $9.9559 \cdot 10^{11}$ m/kg. Low values of the parameters determining the filtration properties are also characteristic of the sludge from the treatment of industrial wastewater.

Because of relatively high hydration sludge the studies were undertaken to determine the susceptibility of this type of sludge to mechanical dewatering. Sludge prior to dewatering process should be subjected to appropriate treatment. This process can change the structure of the sludge and reduce the forces bonding water with surface of sludge flocs.

Therefore, the studies were performed using conditioning of sludge with polyelectrolytes of various ionic character whit dose of 2.1 mg/g TS. The results of tests carried out (Table 2) showed that the best results were obtained when conditioning anionic polyelectrolytes Praestol 2505, Superfloc A 110 and A 130 Superfloc. With their use, large flocs with robust structure and good sedimentation properties were formed.

Table 2

The results of selection of polyelectrolyte type

Type of polyelectrolyte	Dose [mg/g TS]	Results
Praestol 644	2.1	small flocs, undergoing defragmentation, low sediment properties
Praestol 611	2.1	small flocs, undergoing partial defragmentation, low sediment properties
Praestol 2505	2.1	large flocs, non-undergoing defragmentation, well sediment properties
Zetag 63	2.1	small flocs, undergoing defragmentation, low sediment properties
Zetag 47	2.1	small flocs, undergoing defragmentation, low sediment properties
Magnaflock 155	2.1	small flocs, undergoing defragmentation, low sediment properties
Zetag 8846	2.1	small flocs, undergoing defragmentation, low sediment properties
Praestol 2640	2.1	average flocs, undergoing partial defragmentation, low sediment properties
Praestol 2540	2.1	average flocs, undergoing partial defragmentation, low sediment properties
Superfloc A 110	2.1	large flocs, non-undergoing defragmentation, well sediment properties
Superfloc A 150	2.1	average flocs, undergoing partial defragmentation, low sediment properties
Superfloc A 130	2.1	large flocs, non-undergoing defragmentation, well sediment properties

Table 3

The results of selection of polyelectrolyte dose

Type of polyelectrolyte	Dose [mg/g TS]	Results
Praestol 2505	2.1	large flocs, undergoing partial defragmentation, well sediment properties, partially passing through the belt
	3.4	large flocs, non-undergoing defragmentation, well sediment properties, partly passing through the belt
	8.2	large flocs, partial undergoing defragmentation, very quickly sediment properties, does not passing the belt
	15.4	very large flocs, non-undergoing defragmentation, well sediment properties, does not passing the belt
Superfloc A 110	2.1	large flocs, partial undergoing defragmentation,well sediment properties, partially passing through the belt
	3.4	large flocs, partial undergoing defragmentation, well sediment properties, partially passing through the belt
	8.2	large flocs, partial undergoing defragmentation, well sediment properties, does not passing the belt
	15.4	very large flocs, non-undergoing defragmentation, well sedimenting, does not passing the belt
Superfloc A 130	2.1	large flocs, partial undergoing defragmentation, well sediment properties, passing through the belt
	3.4	large flocs, non-undergoing defragmentation, well sediment properties, partially passing through the belt
	8.2	large flocs, partial undergoing defragmentation, well sediment properties, partially passing through the belt
	15.4	very large flocs, non-undergoing defragmentation, well sediment properties, does not passing the belt

In the next stage the most effective polyelectrolytes for the selection of the optimum dose of the reagent in the range of 2.1-15.4 mg/g TS were carried out flocculation tests, the strength test and the sieve test. The results of these tests are presented in Table 3. Analyzing the results of the tests it can be concluded that for lower doses of polyelectrolyte the results were unsatisfactory. The obtained in the test sieve filtrates were turbid and flocs structure was unstable and most of them passed through the belt. The best results in the form of large and robust flocs and a clear filtrate was obtained for doses 8.1 and 15.4 mg/g TS.

In addition, filtration properties of sludge during conditioning polyelectrolytes improved. It was confirmed by shortened capillary suction time. The results of CST varied in the range of 18 to 33 seconds (Fig. 1). It should be noted that an overdose of the reagent adversely affected the filtration properties of the sludge, as indicated by prolonged capillary suction time at the dose of 15.4 mg/g TS. The excess polyelectrolyte increased the viscosity of the liquid sludge, so sludge slowly removed water contained therein. For this reason, the selection of the optimal dose of the reagent both the value CST and structure of flocs should be taken into account. Sludge conditioned by selected polyelectrolyte at a dose 8.2 and 15.4 mg/g TS were tested by mechanical dewatering. In this regard, lab centrifuge and belt filter simulator were applied. As a result of dewatering in the centrifuge a relatively small decrease in the total solids was noted (Fig. 2). The effect dewatering depended on the type of a polyelectrolyte used in conditioning. In case of Praestol 2550 dewatered sludge was characterized by a total solids content of 7.8 and 8.2%. More effective was Superfloc A 130, with the total solids content in the sludge after dewatering at 10.4 and 12.7% respectively, for a dose of 8.2 and 15.4 mg/g TS. Increasing dose of polyelectrolyte did not significantly affect the efficiency of the process.

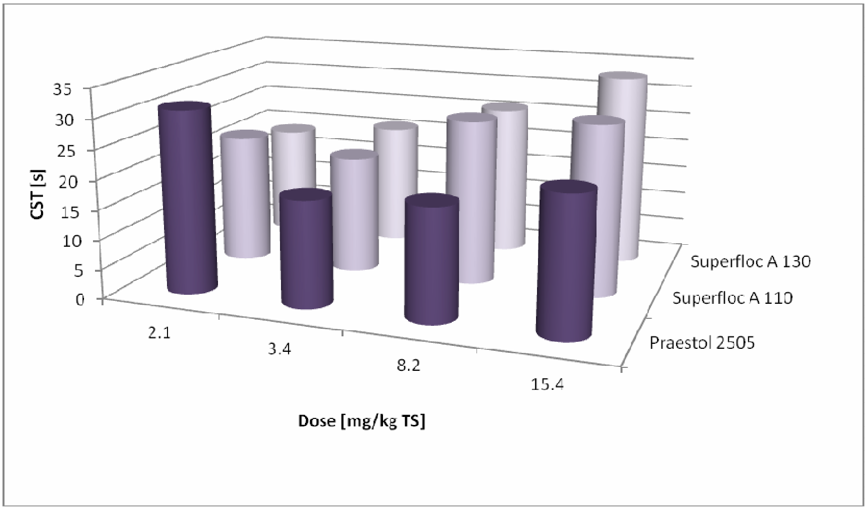

Fig. 1. Changes in CST depending on dose and type of polyelectrolyte

Taking into consideration the results it can be concluded that the use of centrifuges in the process of mechanical dewatering of this type of sludge is inefficient. Significantly better results were obtained when dewatering belt filter simulator was used (Fig. 3). Then dewatered sludge was characterized by a total solids content ranging from 17.7% for the polyelectrolyte Superfloc A 110 and dose 15.4 mg/g TS to 29.5% for polyelectrolytes Superfloc A 110 and Praestol 2550 and the dose 8.2 mg/g TS. In this case, increasing dose of polyelectrolyte resulted in worsening the effects of dewatering.

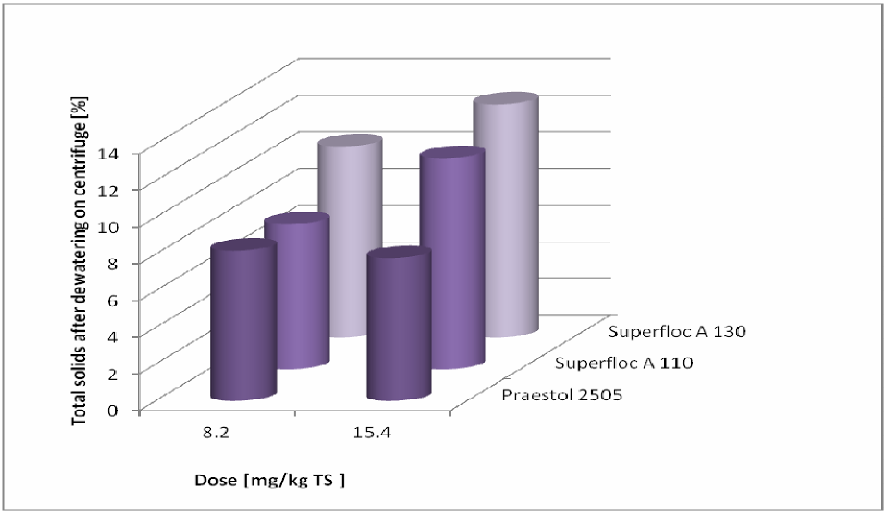

Fig. 2. Changes in total solids after dewatering on centrifuge depending on dose and type of polyelectrolyte

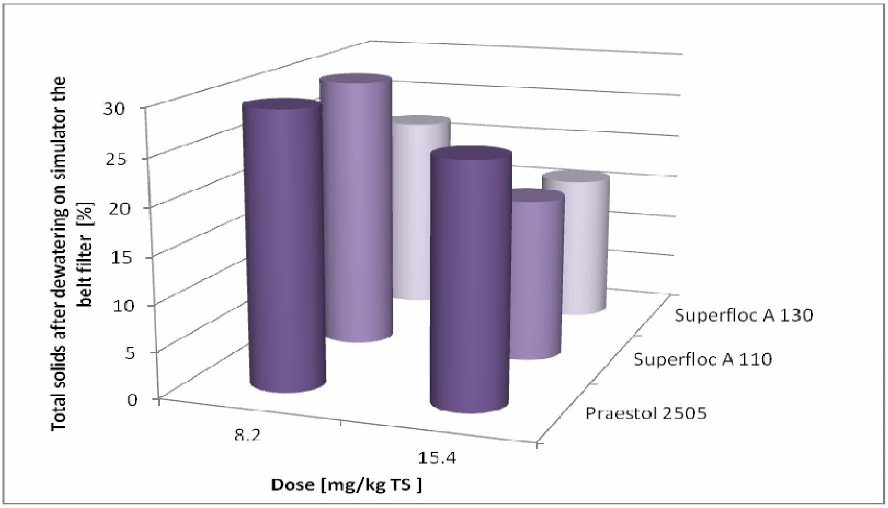

Fig. 3. Changes in total solids after dewatering on belt filter depending on dose and type of polyelectrolyte

Summary and conclusions

Treatment of sewage sludge is an important element of water - sewage management. This is due to the need to remove sludge from sewage treatment plants and its disposal in such a way to reduce their negative impact on the environment. In case of sludge derived from treatment of wastewater from the electroplating industry its disposal is important, because the sludge is characterized by high toxicity caused by inorganic compounds present in wastewater after plating processes. It is important to apply processes to reduce them, which can be implemented in the process of mechanical dewatering. Therefore, the studies were made in order to assess the susceptibility of sludge from the industrial treatment of wastewater to mechanical dewatering.

The sludge prior to dewatering should be subjected to conditioning process. This process improves the structure of the sludge and increases the amount of free water. Process conditioning was conducted based on different types of ion-polyelectrolytes for the equal dose of 2.1 mg/g TS. Test results have shown that the best effective was obtained when the anionic polyelectrolyte were used (Praestol 2505 and Superfloc A 110 and A 130). In the case of these polyelectrolytes prior to the test of mechanical dewatering the optimal dose from 2.1 to 15.4 mg/g TS was determined. Properly selected type of polyelectrolyte and the dose for improvements in the filter characteristics of sludge, increased its susceptibility to dewatering. Sludge conditioned with polyelectrolytes was mechanically dewatered in a centrifuge and in a belt filter simulator. The centrifuged sludge characterized by a relatively low concentration total solid content of 7.8-12.7%. The efficiency of dewatering process was affected by the spin speed and duration of the process. The best results were obtained after 10 min at a speed of 3000 rev./min. Definitely better effect of dewatering occurred when using the belt filter simulator. The dewatered sludge possessed concentration total solids content 17.7-29.5%. The highest degree of dewatering has been achieved with doses of 8.2 mg/g TS of Praestol 2550 and Superfloc A 110. It is worth noting that increasing dose of polyelectrolyte resulted in the worse efficiency of mechanical dewatering. Comparing the results of the mechanical dewatering it was stated that the belt filter is more efficient as indicated by the high degree of dewatering. Definitely worse effect was obtained with the centrifuge, where the centrifugal force is the crucial factor. Satisfactory results dewatering may be obtained with a filter press in which pressure is generated under the influence of the two belts.

Industrial sludge from treatment of electroplating process wastewater can be subjected to mechanical dewatering. However, in order to achieve the expected results the proper preparation of sludge before dewatering, as well as the selection of the appropriate device is necessary.

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ODWADNIALNOŚĆ OSADÓW POCHODZĄCYCH Z OCZYSZCZANIA ŚCIEKÓW GALWANICZNYCH

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Abstrakt: Galwaniczne pokrywanie wyrobów trwalszymi powłokami stanowi ich ochronę lub dekorację. W wyniku tych procesów powstają ścieki technologiczne, które są oczyszczane. Podczas oczyszczania ścieków powstają osady, które stanowiły przedmiot badań. Osady pochodziły z oczyszczalni ścieków znajdującej się przy zakładzie produkującym części samochodowe. Zostały pobrane ze zbiornika szlamowego, poprzedzonego sedymentacją w osadniku lamelowym. W celu określenia ich podatności na odwadnianie w pierwszym etapie dokonano doboru rodzaju i dawki polieletrolitu. W drugim etapie badań kondycjonowane osady poddano próbom mechanicznego odwadniania w wirówce oraz symulatorze prasy taśmowej. Uzyskane wyniki badań wykazały, że najskuteczniejszy wpływ zaobserwowano w przypadku zastosowania polielektrolitów anionowych Praestol 2505 oraz Superfloc A 110 i A 130. W badaniach zastosowano dawki od 2,1 do 3,4 mg/g s.m. oraz od 8,2 do 15,4 mg/g s.m. Zastosowanie zarówno zbyt małej dawki reagenta, jak i przedawkowanie doprowadziło do uzyskania niezadowalających efektów kondycjonowania. Nadmiar polielektrolitu zwiększył lepkość cieczy osadowej, przez co osad wolniej oddawał zawartą w nim wodę. Kondycjonowane wybranymi polielektrolitami osady zostały poddane procesowi mechanicznego odwadniania. W wyniku wirowania otrzymano osad charakteryzujący się zawartością suchej masy maksymalnie 12,7%. Na efektywność procesu odwirowania miała wpływ prędkość wirowania oraz czas trwania procesu. Najlepsze efekty uzyskano dla czasu wynoszącego 10 min oraz prędkości 3000 obr/min. Wyższy stopień odwodnienia wynoszący 29,5% s.m. uzyskano przy zastosowaniu symulatora pracy taśmowej.

Słowa kluczowe: osady ściekowe z przemysłu, odwadnianie mechaniczne, dobór polielektrolitu

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PRO-ENVIRONMENTAL TREATMENT TECHNOLOGY OF INDUSTRIAL BRINES USING CERAMIC MEMBRANES

PROŚRODOWISKOWA TECHNOLOGIA OCZYSZCZANIA SOLANEK PRZEMYSŁOWYCH Z ZASTOSOWANIEM MEMBRAN CERAMICZNYCH

Abstract: The paper presents the results of a multi-stage ultrafiltration process of industrial waste brines with the use of a pilot plant and commercial ceramic membranes. The purpose of the study was to analyse the applicability of ultrafiltration and membranes of various cut-off for the treatment of waste brines and fractionation of proteins contained therein. Research on the membrane process was performed under constant conditions: transmembrane pressure *TMP* = 0.2 MPa, velocity of a saline over the surface of the membrane *CFV* = 6 m/s, the temperature *T* = 25°C using ceramic membranes with a cut-off of 300, 150 and 50 kDa. In tests run in the semi-open ultrafiltration system (continuous discharge of a permeate and retentate recirculation) there were analysed the concentration of protein in permeate and retentate, as well as the recovery of the permeate Q_P. Results of microbiological tests on used brines and permeates after ultrafiltration process performed by an independent testing laboratory are also presented.

Keywords: ultrafiltration, ceramic membranes, industrial brine, fish processing, microbiological analysis

Implementation of the principle of sustainable development into practice in the protection of the aquatic environment requires the use in industrial plants, including food-processing plants, environmental solutions, whose primary task is to close the water loops in order to minimize water consumption and sewage discharge and additionally recovery of secondary raw materials. Fish processing plants are characterized by a very large consumption of water for technological purposes. In the production of salted and smoked fish average consumption of water per 1 Mg of the finished product is approx. 25 m^3, and the production of canned fish reaches up to 60 m^3. At the same time, due to the employment of process brines with a high content of NaCl, large volumes of polluting the environment high-salted wastewater are generated, in which the chloride content reaches up to 20/dm^3. This type of wastewaters is also characterized by the high values of pollutant concentrations such as BOD_5 and COD as well as total suspended solids, TSS, exceeding significantly limits of these indicators set out in the Regulation of the Minister of the Environment on the conditions to be met when discharging wastewater to waters or ground. In the process of treatment of wastewater from fish processing, the biggest problem creates the high content of NaCl, since up to now there is still lack of efficient and cost effective methods of removing chlorides from wastewater to levels required by law [1, 2].

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The proposed global and in-country solutions to this problem involve the use of appropriate technology of used brines reclamation for return to the process and the simultaneous recovery of valuable components. In recent years, more and more common to employ are hybrid technologies consisted of membrane processes as a main step. Within the hybrid technology, membrane techniques are employed as the separation processes - these use pressure membrane processes such as ultrafiltration and inorganic membranes. The main advantage of ultrafiltration in this case is not only a possibility of separation of fat and proteins but also of microbial contamination [3-5].

The purpose of the study was to analyse the applicability of ultrafiltration and the membranes of various cut-offs for treatment of waste brines and rejection of proteins contained in industrial brines. Studies performed under constant process conditions, determined influence of membrane cut-off protein rejection R and recovery coefficient Q_P.

Materials and methods

Research has been accomplished using pilot membrane installation, consisting of basic elements such as a feed tank, a pressure pump and a membrane module of industrial ceramic membranes. The parameters characterizing the membranes are summarized in Table 1. Waste brines from fish processing plant with an average fat content 22 g/kg, concentration of proteins 12 g/dm^3 and sodium chloride 13.5 wt.%, were treated with the use of ultrafiltration. Tests were run in semi-closed ultrafiltration cross-flow system, with continuous discharge of the permeate P, and the retentate R, recycle, in a controlled process maintained in the following conditions: transmembrane pressure, TMP = 0.2 MPa, feed velocity over the surface of the membrane, CFV = 6 m/s and temperature T = 25°C.

Table 1

Characteristics of ceramic membranes used in ultrafiltration tests

Parameter	**Cut-off**	**No of channels**	**Channel hydraulic diameter [mm]**	**Length [m]**	**Filtration area [m^2]**
Value	300 150 50	23	3.5	1.178	0.35

Results and discussion

Multi-stage ultrafiltration tests

Table 2 lists the test results obtained in two series of measurements. In the first series S_1, industrial brine was pre-filtered (bag filters 100, and 1 mm), then the obtained filtrate with a volume of 18 dm^3 was subjected to ultrafiltration with the use of a membrane of 300 kDa. In the last stage of the series S_1, the resulting permeate with a volume of 11.5 dm^3 was subjected to ultrafiltration with the use of a membrane of 150 kDa. In the second series S_2, the filtrate from prefiltration of the initial volume of 22 dm^3 was subjected to ultrafiltration using a 150 kDa membrane and the resulting permeate volume of 11.3 dm^3 was again ultrafiltered using a membrane of 50 kDa. Graphical representation of the industrial treatment of brines in the hybrid filtration-ultrafiltration process is shown in a paper [6]. The protein content in permeates and retentates has been determined based on measurements of TKN (Kjeldahl total nitrogen).

Table 2

Results of experimental two-stage ultrafiltration of industrial brines after prefiltration

Series of measurements	**Membrane cut-off [kDa]**	**UF time *t* [min]**	**Feed volume V_F [dm^3]**	**Permeate volume V_P [dm^3]**	**Permeate recovery $Q_P = V_P/V_F$**	**Average protein content in P after time *t* [g/dm^3]**	**Average protein content in R after time *t* [g/dm^3]**
S_1	300	40	18.0	11.5	0.64	1.97	5.0
	150	20	11.5	6.0	0.52	-	-
S_2	150	75	22.0	11.3	0.51	1.65	3.2
	50	45	11.3	5.0	0.44	1.31	2.1

Results presented in Table 2 show that a two-step ultrafiltration process preceded by a prefiltration leads to the concentration of proteins in the retentates. At the same time, the permeate protein contents have decreased in comparison to the raw brine to a level in the range of 1.97-1.31 g/dm^3, depending on the cut-off of the membrane. Permeates obtained using ultrafiltration process were transparent with good smell. Figure 1 shows photos of brine (feed), permeate after ultrafiltration with a use of 150 kDa membrane, and a retentate after long-term test.

Microbiological analysis

Food industry is very much focused on ensuring the microbiological cleanliness of the processes used. Therefore, in assessing the applicability of the tested membranes for brine treatment, one of the most important criteria, in addition to the technological effectiveness are the results of microbiological tests.

Fig. 1. The samples of raw brine as well as permeate and retentate after ultrafiltration process with a use of 150 kDa membrane [7]

Microbiological tests were performed in two independent laboratories. Testing involved samples obtained from the ultrafiltration process (feed, F_i) and after ultrafiltration (permeate, P_i), for ultrafiltration process with the use of membranes 300 and 150 kDa. Ultrafiltration with the use of membranes 150 and 300 kDa concerned the brines from two different fish processing plants, respectively, F_1 and F_2. Performed microbiological analyses determined the total number of psychrophilic microorganisms at 7 and 20°C as well as number of halophilic microorganisms. Determination of the total number of psychrophilic microorganisms were performed in accordance with a Polish standard PN-90 A-75052/05, while in a case of halophilic microorganisms substrate after Burbianka and Pliszka was used [8].

Table 3

Results of microbiological analysis

Membrane cut-off	Determined microorganisms	Analysed samples	Cell number [cfi/cm^3]
150 kDa	Halophilic	Feed, F_1	$8.6 \cdot 10^2$
		Permeate, P_1	ng
	Psychrophilic, 20°C	Feed, F_1	$2.3 \cdot 10^3$
		Permeate, P_1	ng
	Psychrophilic, 7°C	Feed, F_1	ng
		Permeate, P_1	ng
300 kDa	Psychrophilic, 20°C	Feed, F_2	$9.8 \cdot 10^3$
		Permeate, P_2	ng
	Psychrophilic, 7°C	Feed, F_2	$1.7 \cdot 10^2$
		Permeate, P_2	ng

ng = no growth; cfi = colony-forming individuals

As it is apparent from Table 3, there was no presence of test microorganisms in the ultrafiltration permeates for both membrane 150 and 300 kDa. Decreasing the temperature from 20 to 7°C had a beneficial effect on the microbiological test samples before ultrafiltration (F_1 and F_2), substantially reducing the amount of cells present. While implementing the technology into practice it is strongly recommended that storage of spent brine takes place in the refrigerator.

Conclusions

The aim of the research is to develop pro-environmental regeneration technology of used brines generated at fish processing plants with the use of pressure-driven membrane processes and ceramic membranes, allowing the treatment of brine to a level enabling the recycling to a technological process and recovery of proteins and their hydrolysis products. Pro-environmental and economic aspects of the implementation of such technology in fish processing plants and other salt-using processes make them fully deserving underline. Regeneration of waste brines and their re-use in the process will lead to significant reduction of their consumption. This will reduce the quantity and pollution load discharged to the wastewater treatment plant and translate into lower fees for wastewater management. Simultaneously the production costs associated with the purchase, transportation and storage of fresh brines as well as with waste brine disposal will be substantially reduced.

Literature data analysis and the results of this study indicate that the abovementioned is possible if a hybrid system consisting of prefiltration and ultrafiltration in several steps using membranes with a suitable cut-off is designed and developed. It will be also undoubtedly necessary to identify the optimal process parameters and develop a technological database characterizing performance and selectivity of applied membranes.

Analysis of the research results clearly indicates that a hybrid process composed of the filtration on a pre-filter and a bag filter of 100 and 1 mm followed by several steps of ultrafiltration on ceramic membranes with cut-off of 300, 150 and 50 kDa, allows for protein removal from waste brine to less than 2 g/dm^3 and 100% elimination of psychrophilic microorganisms. Ultrafiltration tests completed in time up to 75 min under constant process conditions: TMP = 0.2 MPa, CFV = 6 m/s at 25ºC have allowed for achievement of the recovery factor of the treated brine, Q_P up to 64%.

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PROŚRODOWISKOWA TECHNOLOGIA OCZYSZCZANIA SOLANEK PRZEMYSŁOWYCH Z ZASTOSOWANIEM MEMBRAN CERAMICZNYCH

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Abstrakt: Przedstawiono wyniki badań wieloetapowego procesu ultrafiltracji zużytych solanek przemysłowych z zastosowaniem instalacji pilotowej oraz komercyjnych membran ceramicznych. Celem badań była analiza możliwości zastosowania ultrafiltracji i membran o różnym *cut-off* do oczyszczania zużytych solanek i frakcjonowania protein w nich zawartych. Badania procesu membranowego wykonano w stałych warunkach:

ciśnienie transmembranowe *TMP* = 0,2 MPa, prędkość solanki nad powierzchnią membrany *CFV* = 6 m/s, temperatura *T* = 25ºC z zastosowaniem membran ceramicznych o cut-off 300, 150 i 50 kDa. W testach ultrafiltracyjnych realizowanych w systemie półotwartym (ciągłe odprowadzanie permeatu i zawracanie retentatu) analizowano zawartość protein w permeatach i retentatach oraz stopień odzysku permeatu Q_p. Przedstawiono również wyniki badań mikrobiologicznych zużytych i oczyszczonych solanek wykonane przez dwa niezależne laboratoria.

Słowa kluczowe: technologie prośrodowiskowe, ultrafiltracja, membrany ceramiczne, solanki przemysłowe, przetwórstwo ryb, analiza mikrobiologiczna

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CONTENT OF POLYCYCLIC AROMATIC HYDROCARBONS IN SOIL FERTILIZED WITH ORGANIC MATERIALS DERIVED FROM WASTE

ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

Abstract: The aim of the research was to determine the influence of fertilization with waste organic materials on the content of polycyclic aromatic hydrocarbons (PAHs) in soil. Samples obtained in the third year of the field experiment were analysed. The field experiment comprised 7 treatments: a non-fertilized soil and a soil fertilized with mineral fertilizers, cattle manure, green waste compost, sewage sludge, compost from sewage sludge and straw as well as with a mixture of sewage sludge and hard coal ash. Maize, which was cultivated for silage, was the test plant. The content of 16 compounds belonging to the group of polycyclic aromatic hydrocarbons (according to the list of the United States Environmental Protection Agency) in the soil was determined using gas chromatography with mass detection, after solid phase extraction. The total content of the 16 PAHs was lower in the soil fertilized with manure and compost from sewage sludge and straw than in the control soil, and higher in the soil fertilized with green waste compost as well as with the mixture of sewage sludge and ash. It was determined that the PAHs content in the soil of the two remaining treatments was close to the content found in the non-fertilized soil. 4-ring compounds constituted the highest share among polycyclic aromatic hydrocarbons.

Keywords: polycyclic aromatic hydrocarbons, sewage sludge, compost

In Poland, application of composts and sewage sludge for fertilization is possible when these materials do not pose a threat connected with an excessive content of heavy metals or the presence of microorganisms and parasites [1, 2]. Currently, however, attention is drawn also to the presence of organic compounds belonging to persistent organic pollutants (POPs) in waste materials. Examples of POPs are: polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and absorbable organic halides (AOX) [3-5]. They are compounds of anthropogenic origin which are carried for considerable distances (thereby occurring in places far away from where they originated). They are characterized by a long half-life period and lipophilic properties. These compounds show mutagenic, carcinogenic, teratogenic, and cytotoxic effects. What is important is that organic pollutants introduced into soils can be, similarly to trace elements, transferred to further links of the soil-plant-animal-human food chain, where they can be accumulated [6].

As it was highlighted above, POPs include, among others, polycyclic aromatic hydrocarbons. They are compounds which have between two and thirteen benzene rings arranged in linear, angle or cluster configurations. Number of rings in a PAH molecule determines compound properties - hydrocarbons with a greater number of rings are less volatile and less water-soluble, but more resistant to biological decomposition. It is

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confirmed by results of research by Banach-Szott et al [7]. The main anthropogenic sources of PAHs include: industry (petroleum refining), combustion of fossil fuels and waste, and road transportation (combustion of fuels as well as abrasion of tyres and asphalt) [3, 6]. Fertilization with PAH-containing materials derived from waste may increase the content of these compounds in soil and plants [8-10].

The research was conducted in order to determine the influence of fertilization with waste organic materials on the content of polycyclic aromatic hydrocarbons (PAHs) in soil. The following organic materials were analyzed for the impact they have: compost from green waste, municipal sewage sludge which was not composted, compost from sewage sludge and wheat straw as well as mixture of sewage sludge and hard coal ash.

Material and methods

Samples obtained in the third year of the field experiment were analyzed. The field experiment was carried out at the experimental station of the University of Agriculture, in Krakow-Mydlniki. The experiment was conducted on an acid soil (pH_{KCl} = 5.40) with grain-size distribution of light clay. Content of trace elements in the soil did not exceed the maximum permissible values established for agricultural use of sewage sludges, neither did the pH_{H2O} value of soil make fertilization with sewage sludge impossible [2]. The total content of 16 PAHs in the soil amounted to 488.3 μg · kg^{-1} d.m., whereas the soil contained:

- 17.5 μg · kg^{-1} d.m. of 2-ring PAHs,
- 88.8 μg · kg^{-1} d.m. of 3-ring PAHs,
- 243.8 μg · kg^{-1} d.m. of 4-ring PAHs,
- 138.2 μg · kg^{-1} d.m. of 5- and 6-ring PAHs.

The experiment was set up in 2008 and continued in the years 2009 and 2010. The field experiment comprised 7 fertilizing treatments (each conducted in 4 replications): non-fertilized soil (control treatment) as well as soil fertilized with mineral fertilizers, cattle manure, compost from green waste, stabilized municipal sewage sludge coming from a mechanical-biological sewage treatment plant, compost from municipal sewage sludge and wheat straw, and with a mixture of sewage sludge and hard coal ash.

Table 1

Content of PAHs in manure and organic materials used for fertilization

PAHs		**Manure**	**Compost from green waste**	**Sewage sludge**	**Compost from sewage sludge and straw**	**Mixture of sewage sludge and ash**
		[μg · kg^{-1} d.m.]				
Number of rings in a PAH molecule	2	478	28.3	1519	4589	7360
	3	37.7	128	2323	424	19,957
	4	n.s.[*]	911	680	3894	371
	5 + 6	n.s.	322	305	21.5	425
Sum of 16 PAHs		516	1389	4827	8929	28,113

[*] n.s. - not stated

Content of trace elements in the organic materials used for fertilization did not exceed the permissible value established for agricultural use of sewage sludges [2]. Among the materials used for fertilization, the lowest content of PAHs was found in manure, and the highest in mixture of sewage sludge and hard coal ash (Table 1). A high content of PAHs in the compost from green waste was due to the type of material used in composting - the compost was generated mainly from waste coming from maintenance of urban green areas.

The PR 39F58 maize of Pioneer was the test plant in all years of the research and it was grown for silage. In the 1st year of the experiment, the following doses of fertilization were used: 160 kg N, 168 kg P_2O_5, and 140 kg $K_2O \cdot ha^{-1}$. To the soil fertilized with manure and organic materials, the whole nitrogen dose was introduced in manure and those materials. Mineral fertilizers (ammonium nitrate, enriched superphosphate and potassium chloride) were used to introduce the nutrient elements to the soil in a treatment fertilized with mineral fertilizers and to equalize the doses of phosphorus and potassium in the soils of the remaining fertilized treatments. 100 kg N, 30 kg P_2O_5, and 110 kg $K_2O \cdot ha^{-1}$, all in the form of mineral fertilizers, were used in the 2nd and 3rd year of the research. Accurate data regarding conditions of conducting the experiment were included in the papers of Tabak and Filipek-Mazur [11, 12].

In the samples, the content of the following 16 compounds belonging to the group of polycyclic aromatic hydrocarbons, according to the list of the United States Environmental Protection Agency (US EPA), was determined: naphthalene, acenaphthene, acenaphthylene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, indeno[1,2,3-cd]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene. The content of PAHs was determined using gas chromatograph with mass spectroscope Varian GC/MS/MS 4000, after solid phase extraction (SPE) using Bakerbond C18 500 mg/3 ml columns. FactorFour VF-5ms capillary column was used. Due to difficulty separating dibenzo[a,h]anthracene (5-ring compound) and indeno[1,2,3-cd]pyrene (6-ring compound), the content of 5- and 6-ring hydrocarbons was presented as a sum. The determination of the content of PAHs in each sample was conducted in two replications. In order to perform calibration, a method of comparison with an outside reference standard was used. Restek 610 PAH Calibration Mix A was chosen as reference standard.

Statistic elaboration of the results was made using Statistica 10 software. A univariate analysis of variance was carried out. Significance of differences between mean values was estimated using the Duncan test ($\alpha = 0.05$).

Results and discussion

After three years of the research, a significantly statistical influence of fertilization with manure, green waste compost and with sewage sludge on the content of 2-ring aromatic hydrocarbons in the soil was found (Table 2). Soil in treatments where the mentioned fertilization was introduced contained 93-141% more 2-ring aromatic hydrocarbons than the control soil. The content of 3- and 4-ring compounds in soil from two fertilized treatments was significantly lower than the content determined in the control soil - 61 and 40% in the soil fertilized with compost from sewage sludge and straw respectively, and 46 and 35% in the soil fertilized with manure. The soil fertilized with the mixture of sewage sludge and ash had 40% more 4-ring PAHs than the control soil, and the soil fertilized with green waste compost had 82% more PAHs. The soil fertilized with the mixture of sewage sludge and ash contained also 57% more 5- and 6-ring PAHs than the non-fertilized soil, and the soil fertilized with manure had 64% fewer of these PAHs.

The total content of the 16 PAHs in the soil of the experimental treatments was between 292 and 736 $\mu g \cdot kg^{-1}$ d.m. Compared with the control soil, the content of the sum of PAHs was lower by 43% in the soil fertilized with manure and by 42% in the soil fertilized with compost from sewage sludge and straw, and higher in the soil fertilized with green waste compost as well as with the mixture of sewage sludge and ash by 43 and 35% respectively. It was determined that the content of PAHs in the soil in two remaining treatments (fertilized with mineral fertilizers and sewage sludge) was close to the content found in the non-fertilized soil.

Table 2

Content of PAHs in soil

Treatment	**Number of rings in a PAH molecule**				**Sum of 16 PAHs**
	2	**3**	**4**	**5 + 6**	
	[$\mu g \cdot kg^{-1}$ d.m. ±SD]				
No fertilization	10.5a[*] ±1.0	98.3cd ±26.7	237.8b ±34.7	167.5bc ±57.0	514.1b ±19.6
Mineral fertilizers	11.6a ±1.5	114.9d ±27.7	245.5b ±10.9	166.7bc ±15.6	538.7b ±8.0
Manure	23.4b ±6.2	53.5ab ±24.3	155.0a ±46.8	60.5a ±18.2	292.4a ±28.0
Compost from green waste	20.3b ±3.9	100.2cd ±32.2	432.2d ±67.0	183.1c ±64.8	735.8d ±14.0
Sewage sludge	25.3b ±6.5	65.1abc ±2.3	295.6bc ±27.1	200.9cd ±15.4	586.9bc ±7.4
Compost from sewage sludge and straw	10.0a ±1.7	38.8a ±3.9	143.3a ±17.5	104.8ab ±26.3	296.9a ±14.9
Mixture of sewage sludge and ash	13.2a ±2.5	86.6bcd ±17.8	333.9c ±86.2	262.8d ±87.5	696.6cd ±23.5

[*] Mean values for parameter in columns marked with the same letters do not differ statistically significantly at $\alpha = 0.05$, according to the Duncan test

Soil in two treatments, one fertilized with green waste compost and one fertilized with the mixture of sewage sludge and ash (the content of the 16 PAHs was 736 and 697 $\mu g \cdot kg^{-1}$ d.m. respectively), was polluted with hydrocarbons. According to criteria proposed by the Institute of Soil Science and Plant Cultivation [6], the pollution was small (II degree). It is not recommended to cultivate special crops designated for the production of food with few harmful substances on such polluted soils.

The content of PAHs in the soil determined in own research did not differ from the literature data. In Poland in 2010, in soils of agricultural use, the mean content of 13 PAHs (according to the US EPA list, without naphthalene, acenaphthylene and acenaphthene) amounted to 558 $\mu g \cdot kg^{-1}$ d.m. (data for 216 measuring points), whereas in the Malopolska province the content of 13 PAHs was between 122 and 4903 $\mu g \cdot kg^{-1}$ d.m. (data for 17 measuring points) [12]. In the measuring point located in Krakow, where the field experiment was conducted, the content of 13 PAHs amounted to 1920 $\mu g \cdot kg^{-1}$ d.m. in 2010, whereas in soils collected from two points located in villages closest to the research site the content of 13 PAHs was 393 and 644 $\mu g \cdot kg^{-1}$ d.m. [13]. In own research, the total content of 13 PAHs in soil was between 267 and 710 $\mu g \cdot kg^{-1}$ d.m.

4-ring compounds constituted the highest share among polycyclic aromatic hydrocarbons determined in the soil (Fig. 1). They constituted between 46 and 59% of all determined PAHs.

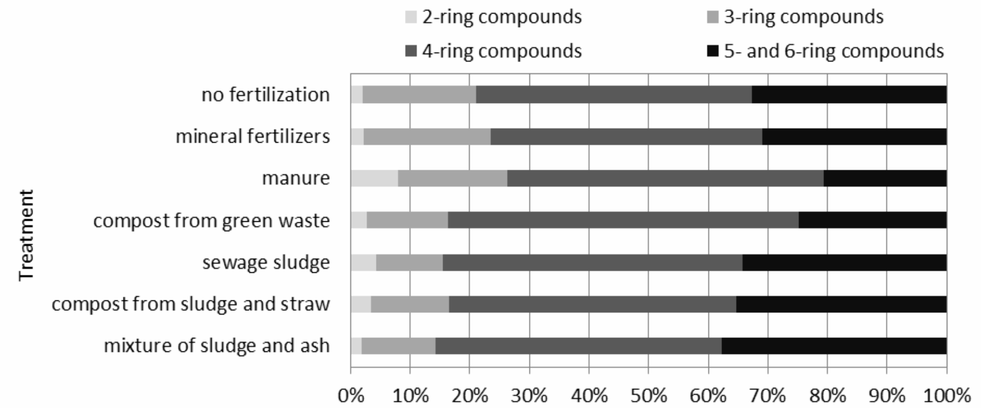

Fig. 1. Share of PAHs with different numbers of rings in sum of 16 PAHs

Conclusions

The carried out research revealed that the mixture of sewage sludge and ash (*ie* material containing the highest amount of polycyclic aromatic hydrocarbons) as well as the compost from green waste had an unbenefical effect on the content of PAHs in the soil. Particularly, fertilization with the compost from sewage sludge and straw did not pose a threat of soil pollution with polycyclic aromatic hydrocarbons.

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ZAWARTOŚĆ WIELOPIERŚCIENIOWYCH WĘGLOWODORÓW AROMATYCZNYCH W GLEBIE NAWOŻONEJ MATERIAŁAMI ORGANICZNYMI POCHODZENIA ODPADOWEGO

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Abstrakt: Celem badań było określenie wpływu nawożenia odpadowymi materiałami organicznymi na zawartość wielopierścieniowych węglowodorów aromatycznych (WWA) w glebie. Analizom poddano próbki uzyskane w trzecim roku doświadczenia polowego obejmującego 7 obiektów: glebę nienawożoną oraz nawożoną nawozami mineralnymi, obornikiem bydlęcym, kompostem z odpadów zielonych, osadem ściekowym, kompostem z osadu ściekowego i słomy pszennej oraz mieszaniną osadu ściekowego i popiołu z węgla kamiennego. Rośliną testową była kukurydza uprawiana na kiszonkę. Zawartość 16 związków z grupy wielopierścieniowych węglowodorów aromatycznych (według listy Amerykańskiej Agencji Ochrony Środowiska) w glebie oznaczono techniką chromatografii gazowej z detekcją masową po ekstrakcji do fazy stałej. Gleba nawożona obornikiem i kompostem z osadu ściekowego i słomy charakteryzowała się mniejszą łączną zawartością 16 WWA od gleby kontrolnej, natomiast gleba nawożona kompostem z odpadów zielonych oraz mieszaniną osadu ściekowego i popiołu - zawartością większą. W glebie pozostałych dwóch obiektów oznaczono zawartość WWA zbliżoną do stwierdzonej w glebie nienawożonej. Wśród wielopierścieniowych węglowodorów aromatycznych największy udział stanowiły związki 4-pierścieniowe.

Słowa kluczowe: wielopierścieniowe węglowodory aromatyczne, osad ściekowy, kompost

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Marcin K. WIDOMSKI[1], Witold STĘPNIEWSKI[1] and Rainer HORN[2]

HYDRAULIC PROPERTIES OF CLAY LINERS OF WASTE LANDFILLS COMPACTED AT VARIOUS WATER CONTENTS

WPŁYW WILGOTNOŚCI ZAGĘSZCZANIA MATERIAŁÓW ILASTYCH NA WŁAŚCIWOŚCI HYDRAULICZNE PRZESŁON MINERALNYCH SKŁADOWISK ODPADÓW

Abstract: According to the actual standards, municipal landfill cells, as highly dangerous to the natural environment, have to be isolated from the environment by liners in order to prevent the migration of anthropogenic pollutants. The properly prepared mineral liners sealing the top, sides and bottom of landfill limiting water infiltration to waste body and leachate seepage are the popular manner of landfills isolation. The mineral liners are usually constructed of compacted clay soils to obtain, the required value of the sealing layer saturated hydraulic conductivity lower than $1 \cdot 10^{-9}$ m s^{-1}. The value of hydraulic conductivity of saturated soil is directly affected by the molding water content during compaction. Additionally, the sustainability of clay liners is highly related to its shrinkage and swelling properties. This paper presents researches concerning the effects of molding water content of selected clay soil on saturated hydraulic conductivity and shrinkage/swelling properties of compacted soil as well as hydraulic properties of the top sealing liner, constructed according to the actual standards, of compacted clay material. Range of our studies covered the laboratory and field measurements as well as numerical modeling. Saturated hydraulic conductivity under the natural field conditions was measured by BAT probe, GeoNordic, hydraulic conductivity of the compacted clay soils was tested in the laboratory by Humboldt Mfg. Co. permeameters for compacted soils, according to ASTM D5856. Water retention characteristics of compacted soil in range of 0-15 bar were determined by application of sand box and pressure chambers with ceramic plates methods. The assessment of hydraulic properties of liner made of clay materials was performed for the 2012 hydrologic year by the method of numerical modeling of infiltration process for a selected section of landfill top cover constructed in Rastorf, Germany, adjusted to Polish standards. The numerical calculations were performed in FEFLOW, DHI-WASY modeling software.

Keywords: clay materials, mineral liners, hydraulic conductivity, numerical modeling

Introduction

Landfilled municipal wastes pose a considerable threat to the natural environment due to the possible migration of numerous pollutants to soil and water, especially by leachate seepage. Generation of leachate is triggered by infiltration of surface water, originated form precipitation and snow cover melting, entering the waste body. Thus, negative environmental impact of landfills depends on the efficiency of limiting the pollution by the applied techniques of sealing [1].

Prevention of surface water infiltration and leachate migration to soil-water environment is realized by barriers, known as liners, based on natural and geosynthetic materials. One of the most popular and durable solution are compacted mineral clay liners meeting the requirements of the local standards [2, 3]. These barriers are constructed of natural clays of permeability capable to meet the required value of hydraulic conductivity [4, 5], which should be lower than $1 \cdot 10^{-9}$ m s^{-1} in the European Union. The saturated

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hydraulic conductivity of clayey soils under natural conditions may be higher than the above value [6-8] so the application of compaction process may be required. The compaction increases the resistance of soil to water flow, significantly reducing the saturated hydraulic conductivity of soil [9], however, the degree of reduction depends on the applied molding water content of the soil. So the molding water content becomes one of the most important factors influencing the hydraulic characteristics of compacted clay liner [10-14]. On the other hand, molding water content affects also the swelling and shrinking properties of clays, influencing the sustainability of the liner [15-17]. Higher shrinking potential results in a significant risk of liner cracking, thus, increase of its permeability. This paper presents an attempt of determination of the effects of soil molding water contend on its saturated conductivity, shrinking and swelling potentials and finally the hydraulic properties of the top sealing liner, constructed according to the actual standards.

Materials and methods

The presented studies were focused on mineral clay material sampled in Lazek Ordynacki, approx. 90 km south of Lublin, Poland. The basic characteristics of sampled soil are presented in Table 1.

Table 1

Basic characteristics of the clay material sampled in Lazek Ordynacki, Poland

Particle fraction name	Sand [%]	4.5
	Silt [%]	51
	Clay [%]	44.5
Solid particle density [Mg m^{-3}]		2.614
Bulk density [Mg m^{-3}]		1.693

The particle size distribution of the soil was determined by the standard sedimentation method according to PN-B-04481:1988 [18], solid particle density was measured in le Chatelier flask and gravimetric water content was obtained by the standard weight method according to ASTM C566-13 [19]. The saturated hydraulic conductivity of the tested soil under natural, undisturbed conditions was measured by the field permeameter for fine grained soils GeoN by Geo Nordic, Stockholm, Sweden. Laboratory measurements of saturated conductivity of the soil compacted at various water contents were performed in the permeameters for compacted soils by Humboldt Mfg. Co, USA. The H-4145 compaction permeameters and the falling water head method of measurements, meeting requirements of ASTM D5856-95 [20], were applied to our studies. The soil was compacted, with different molding water contents, according to PN-B-04481:1988 [18]. The following values of molding water contents (by weight) were applied during our laboratory studies: 17, 19, 21 and 23%. Water retention capabilities of the compacted clay material were tested in pressure range 0-15 bar by the standard sand box (IMUZ, Lublin, Poland) and pressure chambers with ceramic plates by Soil Moisture, Santa Barbara, USA. Numerical modeling of hydraulic efficiency of a mineral liner constructed of the compacted clay material was performed by FEFLOW, WASY-DHI, Germany modeling software. The developed two dimensional model represented a 10 m wide section of mineral liner of 2 m thickness, required by the actual Polish and European standards [2, 3], consisting of three layers: clay sealing layer of 0.5 m thickness, sand drainage layer of 0.5 m and soil recultivation layer of thickness equal to 1.0 m. The applied slope shape reflected morphology of the liner in Rastorf, Germany. Top surface of modeled liner was assumed as covered by perennial grass mixture. The prepared model consisted of 5965 nodes and 11549 elements. The developed model was presented in Figure 1.

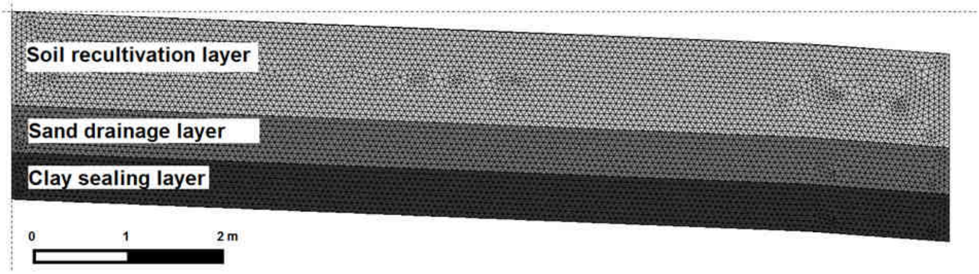

Fig. 1. Developed model of the selected section of municipal landfill top liner

Numerical calculations of the two dimensional water flow in FEFLOW were based on standard forms of Darcy's and Richards' equations [21-23]:

$$\boldsymbol{q}_i = -\boldsymbol{K}_{ij} \frac{\partial h}{\partial x_j}$$

$$\frac{\partial h}{\partial t} = -\frac{\partial \boldsymbol{q}_i}{\partial x_j} \mp Q$$

where: $\boldsymbol{q}_i$ - groundwater flux vector [m s^{-1}], h - hydraulic potential [m], t - time [s], $\boldsymbol{K}_{ij}$ - hydraulic conductivity tensor, $i, j = 1, 2$ [m s^{-1}], Q - sink or source term [s^{-1}].

Mathematical description of water retention curve assumed to our simulations was presented by van Genuchten [24]:

$$\theta = \frac{\theta_s - \theta_r}{[1 + (Ah)^n]^m} + \theta_r$$

where: θ_s - saturated volumetric water content [m^3 m^{-3}], θ_r - residual volumetric water content [m^3 m^{-3}], $\theta_r = 0$ m^3 m^{-3}, h - hydraulic potential [m], A - water retention curve fitting parameter [m^{-1}], n, m - dimensionless water retention curve fitting parameters, $m = 1 - n^{-1}$.

Hydraulic conductivity of unsaturated soils K was calculated in the presented model according to van Genuchten's formula [24]:

$$K = K_s S_e^l \left[1 - \left(1 - S_e^{\frac{1}{m}}\right)^m\right]^2$$

where: K_s - saturated hydraulic conductivity [m s^{-1}], l - dimensionless fitting parameter, $l = 0.5$ [23], S_e - dimensionless effective saturation defined as:

$$S_e = \frac{\theta - \theta_r}{\theta_s - \theta_r}$$

Characteristics of sand and recultivation layer assumed to modeling are presented in Table 2. The isotropic clay and sand soil were assumed to our calculations due to the developed small scale model [25].

Table 2

Soil characteristics for drainage and cultivation layers assumed to modeling

Parameter	Recultivation layer	Sand drainage
Saturated hydraulic conductivity [m s^{-1}]	$0.02 \cdot 10^{-4}$	$2.0 \cdot 10^{-4}$
Saturated water content q_s [m^3 m^{-3}]	0.29	0.37
Residual water content q_r [m^3 m^{-3}]	0	0.11
Water retention curve parameter A [m^{-1}]	7.645	2.3
Water retention curve parameter n [-]	1.104	7.7
Anisotropy ratio a [-]	0.17	1
Anisotropy rotation angle f [deg]	90	0

Numerical modeling of water infiltration through the mineral liner required assumption of the necessary initial and boundary conditions. The initial condition was assumed as 90% liner's soil saturation, $S = 0.9$. The bottom boundary condition was assumed as the constant gradient type Neumann condition of value equal to saturated hydraulic conductivity of the soil in sealing layer. Such as boundary condition reflects the undisturbed free water drainage, *ie* gravitational seepage to the lower domain. The Neumann type top boundary condition assigned to upper limit of the model reflected water flux entering and leaving the modeled domain. The daily values of water flux were based on measured and calculated daily precipitation, interception, evapotranspiration and surface runoff for municipal landfill in Rastorf, Germany for 2012 hydrologic year.

Results and discussion

The results of saturated hydraulic conductivity measurements as well as bulk density, and water retention characteristics according to van Genuchten model for the applied molding water contents are presented in Table 3.

Table 3

Saturated hydraulic conductivities, bulk densities and water retention parameters of the soil dependently on molding water content

Parameter	Molding water content [% by weight]			
	17	19	21	23
Saturated hydraulic conductivity [m·s^{-1}]	$1.00 \cdot 10^{-10}$	$7.33 \cdot 10^{-11}$	$3.69 \cdot 10^{-11}$	$3.21 \cdot 10^{-11}$
Soil bulk density after compaction [Mg m^{-3}]	1.66	1.70	1.71	1.70
Bulk density after swelling [Mg m^{-3}]	1.52	1.59	1.63	1.60
Soil bulk density after shrinkage [Mg m^{-3}]	1.86	1.97	1.98	2.02
Saturated water content q_s [m^3 m^{-3}]	0.365	0.350	0.346	0.350
Water retention curve parameter A [m^{-1}]	0.105	0.928	0.675	0.100
Water retention curve parameter n [-]	1.197	1.123	1.116	1.155

The results presented in Table 3 show a clear decrease of saturated hydraulic conductivity of clay resulting from the increase of molding water content. All tested cases of compaction with 17, 19, 21 and 23% water content allowed to achieve the values of saturated hydraulic conductivity of clay sealing layer lower than required by the standards [2, 3]. The obtained values of K_s are one or even two orders of magnitude lower than the required. The observed bulk densities of compacted clay show that the maximum value of bulk density, identifying the highest possible degree of compaction, was achieved for molding water content of 21%. The highest swelling potential (difference between soil bulk density and bulk density after swelling) equal to 0.14 Mg m^{-3} was observed for the lowest molding water content applied. On the other hand, the highest shrinkage potential equal to 0.32 Mg m^{-3} was noted for the highest molding water content applied. Taking into account that high shrinkage potential may trigger cracking which significantly increases hydraulic conductivity of soil, it should be suggested that compaction of clay minerals should be performed on the left, "dry", side of Proctor curve. In our case, molding water content between 17 and 21% seems to be suitable.

The results of numerical calculations of water seepage through a 10.0 m section of liner utilizing clay compacted at various molding water content as sealing layer are presented in Figure 2. The results presented in Figure 2 show that hydraulic properties of the mineral clay liner as a barrier for pollutants propagation made of the compacted clay directly depend on the applied molding water content. The lower the molding water content, the higher saturated hydraulic conductivity and the higher infiltration rate for the same upper boundary condition. The observed calculated decrease of unit yearly seepage volume per 1 m^2 was from $4.65 \cdot 10^{-5}$ m^3 to $1.8 \cdot 10^{-6}$ m^3. Figure 2 shows also that there is no significant difference in sealing capabilities after reaching the maximum bulk density during the compaction process.

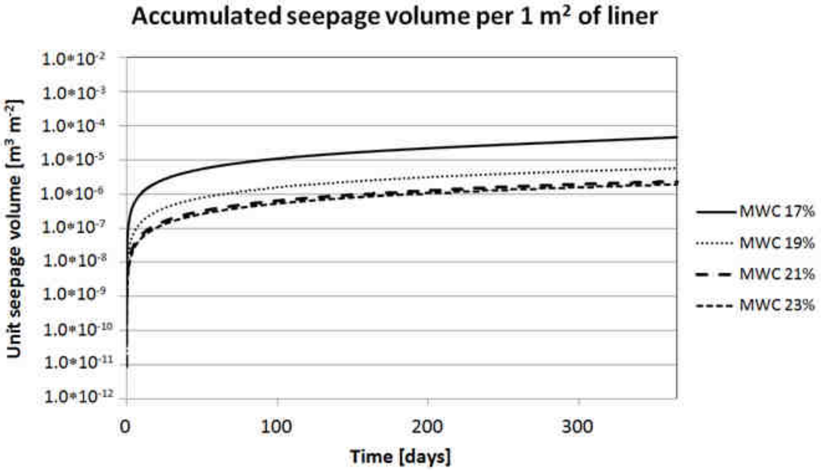

Fig. 2. Calculated yearly cumulative volume of seepage through the bottom boundary of mineral liner made of the clay soil compacted at different water contents (MWC)

Summary and conclusions

Our studies are in agreement with literature proving a direct relation between molding water content applied during compaction of clay and its saturated water conductivity. We observed a decrease of saturated hydraulic conductivity of compacted clay, from $1.00 \cdot 10^{-10}$ to $3.21 \cdot 10^{-11}$ m s^{-1}, due to increase of applied molding water content from 17 to 23%. Additionally, the modeled decrease of seepage percolating through the top liner for the same range of molding water content variability reached one order of magnitude. However, it must be underlined that according to the significant increase of shrinkage potential for values of molding water content higher than value corresponding to the maximum bulk density obtained, the clay utilized in construction of sealing layer should be compacted on the left, dry side of Proctor's curve, below the maximum bulk density. Otherwise, the possibility of soil cracking, reducing the sealing properties of the liner and increasing the possible seepage becomes significant. The above shows that selection of the proper molding water content during construction of the municipal landfill cell liner of the compacted clay material is crucial because it may significantly influence the efficiency of the sealing preventing migration of the pollutants into the natural environment. The lacking validation of our simulation calculations causes that our modeling studies should be treated as preliminary.

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WPŁYW WILGOTNOŚCI ZAGĘSZCZANIA MATERIAŁÓW ILASTYCH NA WŁAŚCIWOŚCI HYDRAULICZNE PRZESŁON MINERALNYCH SKŁADOWISK ODPADÓW

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Abstrakt: Zgodnie z aktualnymi wymogami prawnymi, składowiska odpadów jako szczególnie niebezpieczne dla środowiska muszą być izolowane przesłonami w celu zapobiegania rozprzestrzeniania się zanieczyszczeń antropogenicznych. Jednym ze sposobów zapewniania izolacji składowisk są odpowiednio przygotowane i zagęszczone przesłony mineralne, zabezpieczające pokrywę oraz dno i boki składowiska. Przesłony mineralne są najczęściej wykonywane z odpowiednio zagęszczonych gruntów ilastych, tak aby przepuszczalność hydrauliczna warstwy ekranującej była niższa niż $1 \cdot 10^{-9}$ $m \cdot s^{-1}$. Wartość współczynnika przewodnictwa wodnego gruntu w stanie pełnego nasycenia zależy bezpośrednio od wilgotności ośrodka porowatego w czasie zagęszczania. Dodatkowo, żywotność i efektywność przesłon ilastych jest bezpośrednio uzależniona od charakterystyki skurczu i pęcznienia materiału ilastego. Niniejsza praca przedstawia próbę określenia wpływu wilgotności zagęszczania wybranego gruntu ilastego na przepuszczalność w stanie pełnego nasycenia, potencjał skurczu i pęcznienia gruntu oraz właściwości hydrauliczne przesłony składowiska odpadów wykonanej z zagęszczonego gruntu ilastego, zgodnie z obowiązującym stanem prawnym. Zakres pracy obejmował badania laboratoryjne, terenowe oraz modelowe. Przewodnictwo hydrauliczne gruntów w stanie naturalnym określono za pomocą polowej sondy BAT, GeoNordic, przewodnictwo zaś w stanie pełnego nasycenia po zagęszczeniu wyznaczono za pomocą przepuszczalnościomierzy Humboldt Mfg. Co. do gruntów zagęszczonych wg ASTM D5856. Charakterystykę retencyjną zagęszczonych gruntów w zakresie 0-15 bar wyznaczono za pomocą metody bloku pyłowego oraz komór ciśnieniowych z płytami ceramicznymi. Ocenę właściwości hydraulicznych przesłon wykonanych z badanych materiałów ilastych zrealizowano dla roku hydrologicznego 2012 poprzez modelowanie numeryczne procesu infiltracji przez wybrany fragment przykrycia składowiska odpadów w Rastorf, Niemcy, dostosowany do polskich wymagań prawnych. Badania symulacyjne przeprowadzono za pomocą programu obliczeniowego FEFLOW, DHI-WASY.

Słowa kluczowe: materiały ilaste, przesłony mineralne, przewodnictwo hydrauliczne, modelowanie numeryczne